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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV MARCH 1960 No. 3

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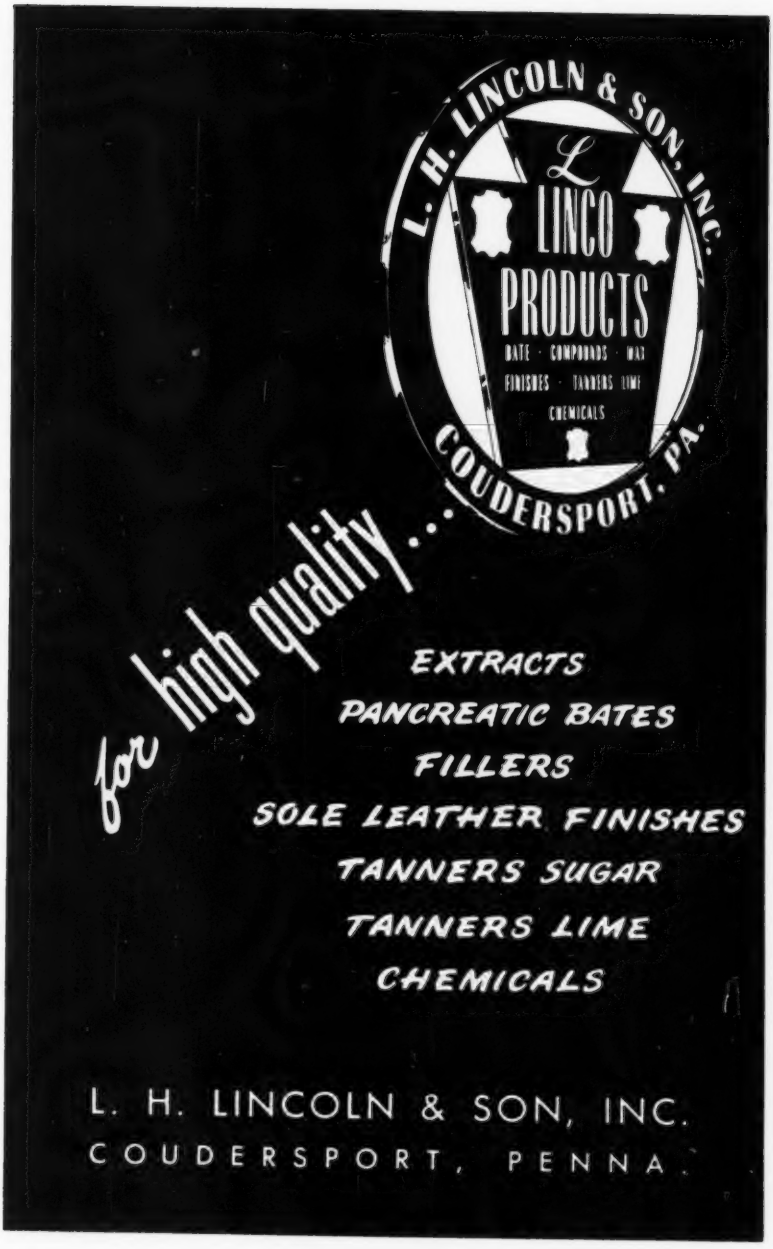
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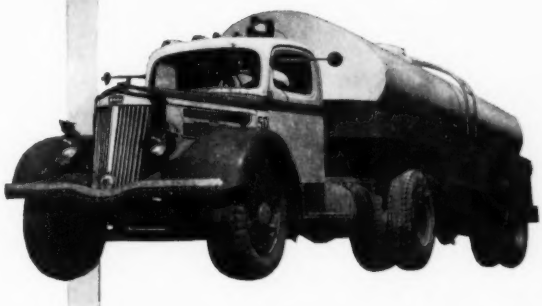

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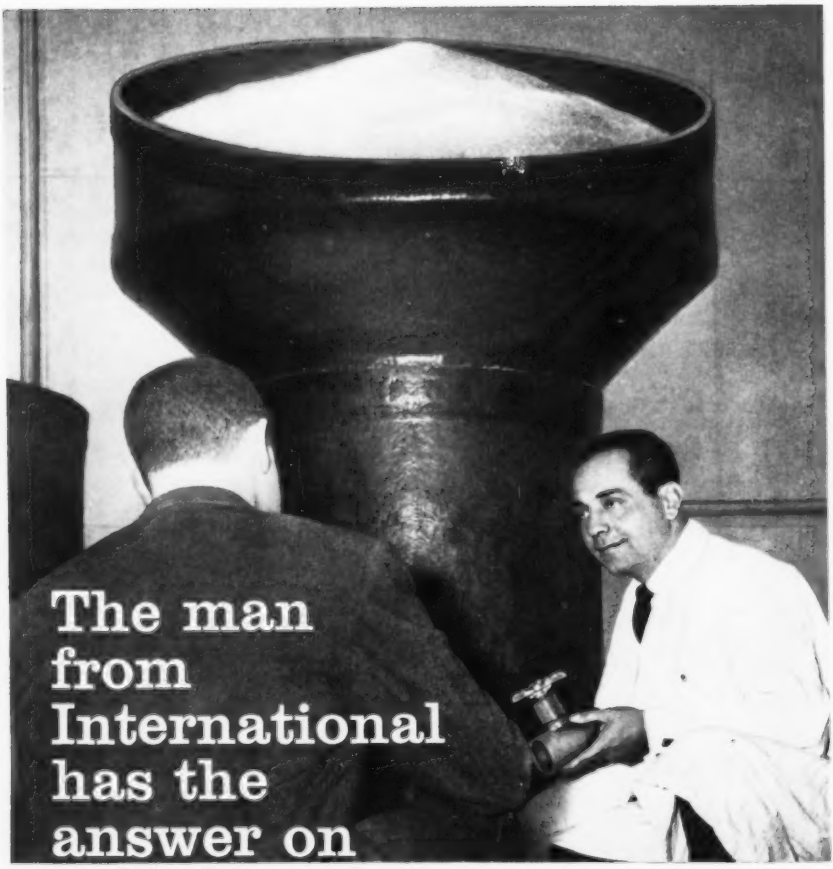

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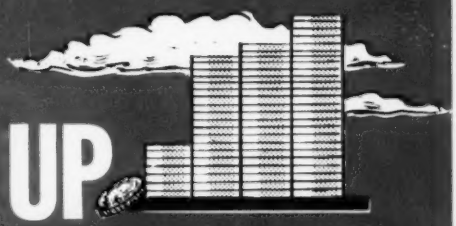

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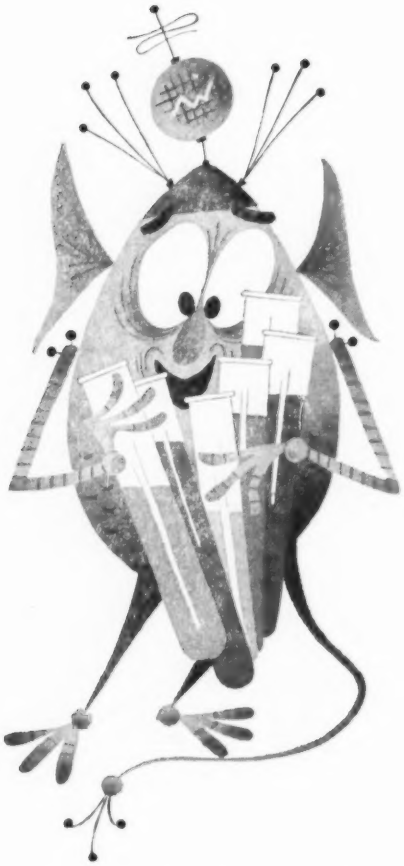

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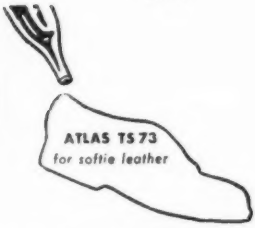

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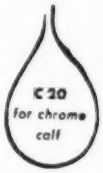

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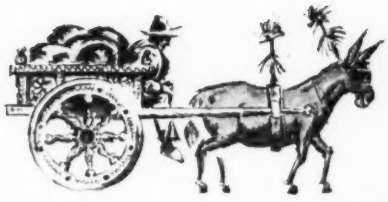

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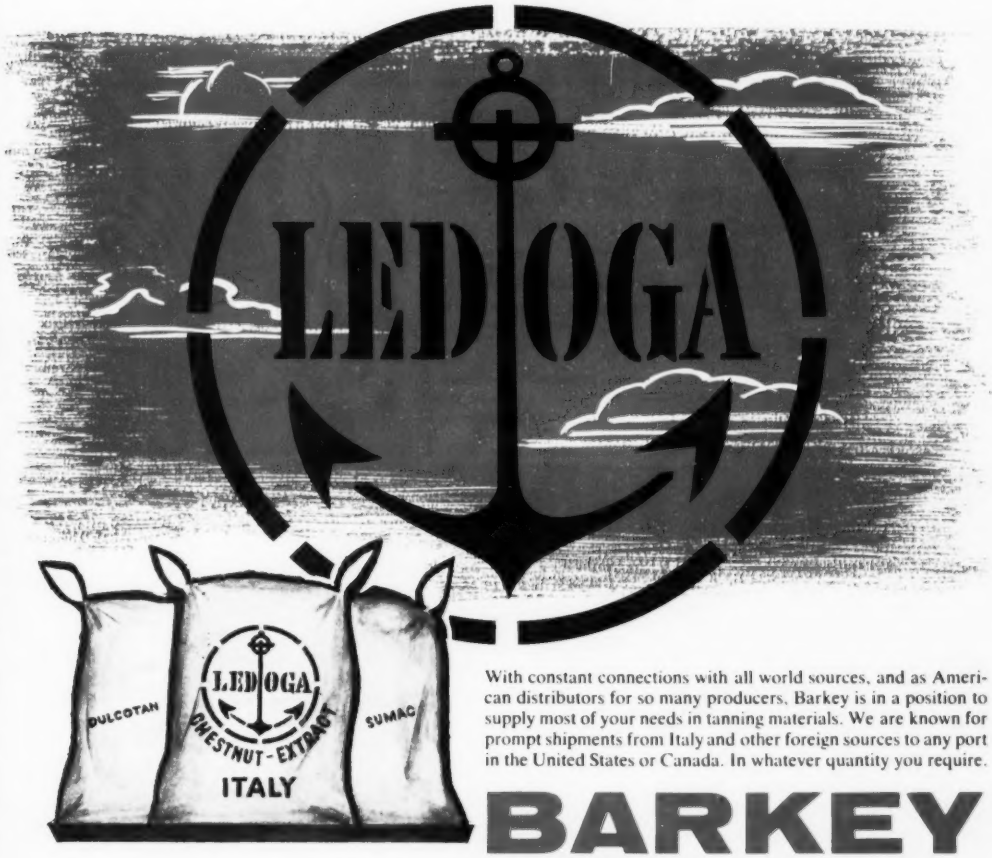

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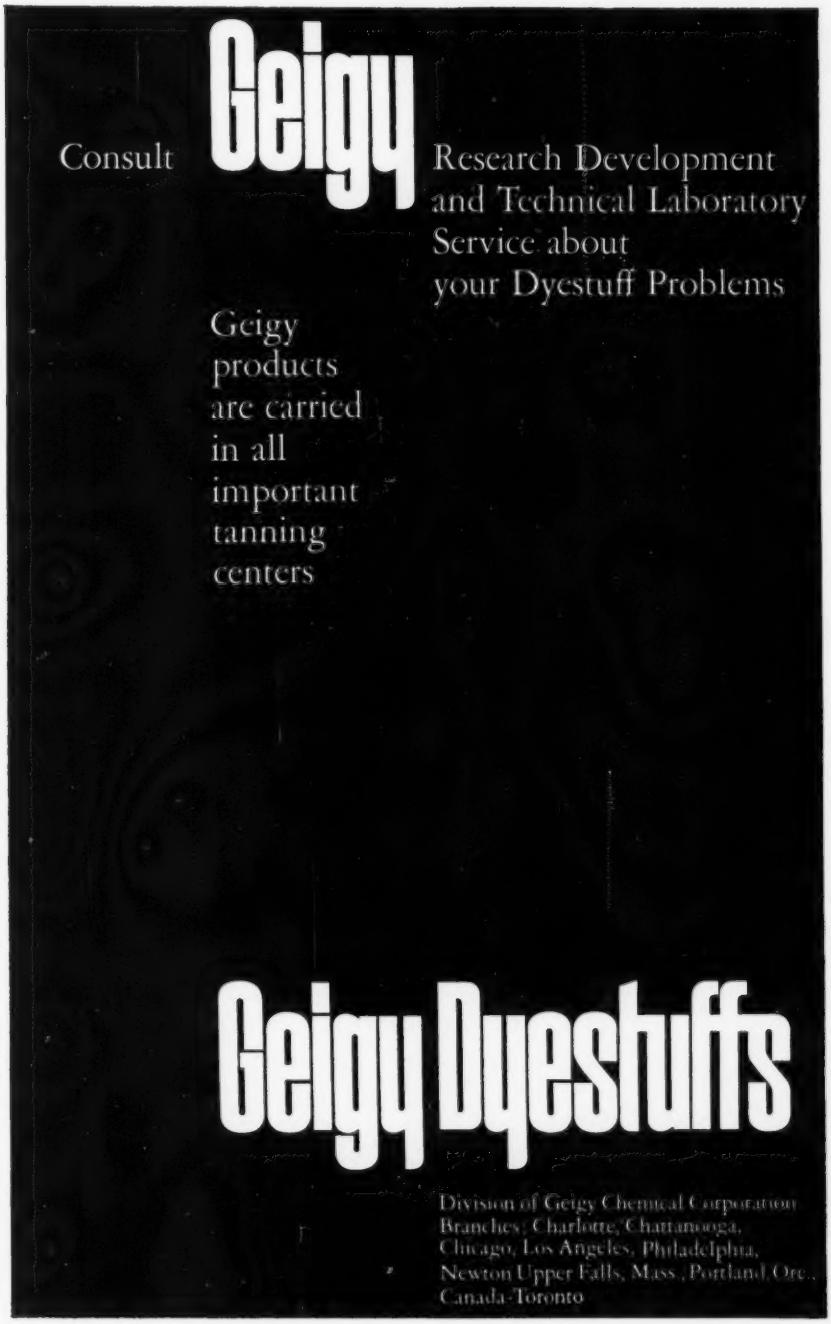
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THE ISOLATION OF ELASTIC TISSUE OF ANIMAL SKIN*

CONRAD L. ORNES AND WILLIAM T. RODDY

Tanners' Council Research Council
University of Cincinnati
Cincinnati 21, Ohio

ABSTRACT

In recent years the behavior of the elastic tissue of animal skin has been under investigation to elucidate its properties. These investigations will be reviewed, and methods of isolation of the elastic tissue from skin and leather will be presented. The isolation methods developed and staining techniques previously developed can be used to determine the modification in the elastic tissue brought about by the various chemicals used in processing skin into leather.

—×—×—

INTRODUCTION

The elastic tissue of animal skin has been studied by many investigators, and a comprehensive review of the occurrence, preparation, and general properties was given by Highberger (1). In this review he mentions that elastic tissue occurs in very small quantities in the skin, the largest amounts being found in the grain layer.

It was reported by Roddy and O'Flaherty (2) that the elastic tissue of calfskin was reduced in amount from that in the fresh skin, but not completely removed, when the stock was processed and finished as chrome-tanned or vegetable-tanned leather. Observations were also made on the appearance of *ligamentum nuchae* (the elastic tissue neck ligament of a calf) which was given the equivalent of a tannery process. Even when the tissue was processed as a particle size obtained by grinding through the finest-mesh screen on the Micro-Wiley Mill, the finely divided elastic tissue particles became hard and harsh when dried from any stage in process, were the consistency of hard wood particles when dried after vegetable tanning, and were similar to glass particles in hardness when chrome-tanned and dried.

*A report of work done in part under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Eastern Utilization Research and Development Division of the Agriculture Research Service. Presented at the Fifty-fifth Annual Meeting, Mackinac Island, Michigan, June 16, 1959.

Hoover *et al.* (3) recently have been able to isolate the grain layer of bovine skin and found it to have properties closely related to those of elastic tissue. The yield of their isolated material was essentially the same per unit area of skin for both calfskin and steerhide.

In further work on the network structure of elastin in the grain layer of cattlehide Mellon and Korn (4) showed by horizontal sectioning and chemical fractionation of the sections that the elastin was a three-dimensional network which extended through the thickness of the grain structure. It was shown that the condensed membrane layer obtained was due to the collapse of this network. They further indicated that a maximum concentration of elastin occurs at about one-third the depth of the grain layer and that commercial trypsin was able to dissolve this elastin network from the surface layers. They used a technique whereby the elastin was separated from the skin collagen by extraction with 0.1*N* sodium hydroxide for 16 hours; then the residue was resuspended in fresh alkali for one hour, after which time it was neutralized and centrifuged. The residue was then suspended in water and autoclaved for 2 hours at 23 pounds steam pressure. After it was cooled and centrifuged, the gelatin extract was decanted, and total nitrogen was determined on the extract and the residue. The elastin nitrogen averaged approximately 2% of the total nitrogen for the epidermal area of the hide.

In a private communication (5) it was requested that limed, unhaired calfskin which was treated with a high trypsin bate be examined in cross section to see if the stock so treated had all of the elastic tissue removed by the treatment. The cross sections of the stock when stained with Weigert's Elastic Tissue Stain showed only fragments of elastic tissue in the blood vessels in the center of the corium, which would indicate that the treatment had removed most of the elastic tissue. However, there was the possibility that the elastic tissue might still be present and its staining characteristics altered. To determine by chemical analyses just how much elastic tissue was present in limed stock before bating and the effect of using strong enzyme action to remove the elastic tissue, the present study was undertaken.

Tancous (6), using her previously developed fractionation technique for determining protein fractions of animal skin, has shown that the purifying action of the normal beamhouse procedure will remove practically all of the nonfibrous protein material from calfskin. She obtained a fraction consisting of elastin and hair-root debris amounting to only 2.2% of the total skin protein. Stubbings (7), in attempting to separate these two components, after using a similar fractionation scheme, found that the use of strong sodium sulfide to dissolve the hair residue also dissolved about 15% of the elastin.

Attempts have been made in this laboratory to purify the elastin-keratin residue by dissolving the elastin component by means of enzymes. However, blood vessels are extremely resistant to enzyme action and will always leave a residue of elastin under any practical tannery conditions. In addition, difficulties are encountered in rehydrating the dried residues.

In the present study a measure of removal of elastin from limed, unhaired, and fleshed stock by means of enzyme action was desired. The hair-root residue in any small area of a skin is quite constant as shown by microscopic examination of cross sections. By relating the weight of elastin-keratin residue to the dry weight of skin it is thus possible to follow the reduction in percentage weight of residue brought about by various treatments with the assurance that such reduction is due mainly to elastin removal.

To indicate what occurs to the elastic tissue of animal skin during process it is possible to follow the changes by microscopic examination of stained sections of the skin or by dissolving the collagenous tissue and determining the amount of elastic-tissue residue. For the purpose of orientation the following section on the histology of skin, both untreated and treated, is given.

MICROSCOPIC EXAMINATION

When cross sections or sections cut in a plane parallel to the hair side are stained with Weigert's Elastic Tissue Stain, the following photomicrographs can be made of the elastic tissue of the skin. In viewing these sections it is to be kept in mind that the elastic tissue is present as a network surrounding the hair follicles in the epidermal area and as part of the arteries found throughout the skin. Such arteries are responsible for the so-called veins which are unsightly on the finished leather when prominent.

In Fig. 1 a cross section of fresh calfskin stained with Weigert's Elastic Tissue Stain is shown. In this cross section the elastic tissue is seen mainly in the epidermal area and on the flesh side. It is located in the epidermal area as a basketlike network which extends from the epidermis to the sweat

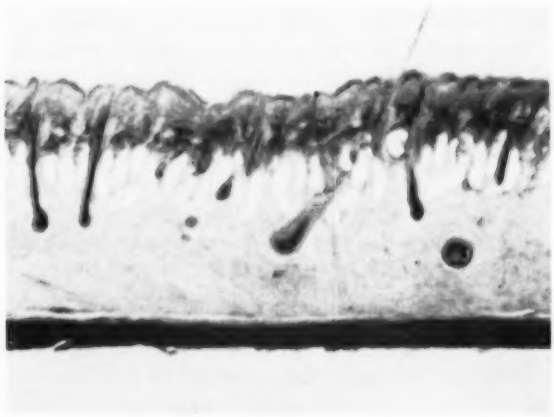

FIGURE 1.—Cross section of fresh calfskin stained with Weigert's Elastic Tissue Stain.

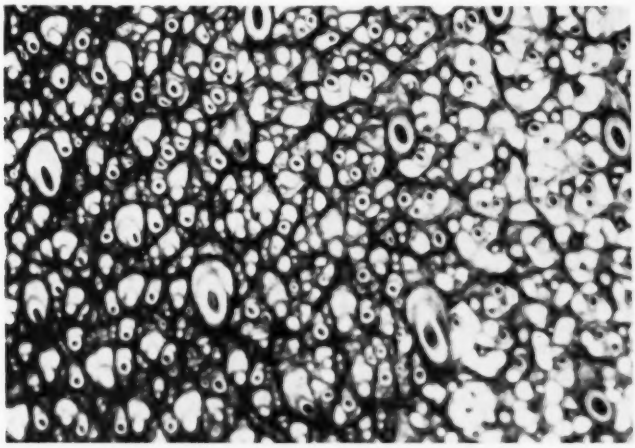

FIGURE 2.—Section cut in horizontal plane of fresh calfskin stained with Weigert's Elastic Tissue Stain.

FIGURE 3.—Cross section of the epidermal area of fresh calfskin stained with Weigert's Elastic Tissue Stain.

glands surrounding each hair pocket. Figure 2 is a section cut in a horizontal plane with the portion on the left side showing the network of the elastic tissue surrounding each hair pocket and the right-hand portion the sweat glands. The only elastic tissue in this area is in the arteries running between the sweat glands. For a more detailed picture of the elastic tissue in the epidermal area Fig. 3 is shown. The elastic tissue is more dense in the oil gland region and shows finer fibers as the tissue attaches to the epidermis. At the top of the oil glands are three arteries cut in cross section containing elastic tissue as part of their walls.

In a cross section of fresh steerhide as shown in Fig. 4 the elastic tissue is similar to that seen in calfskin, being located in the epidermal area and on the flesh side when stained with Weigert's Elastic Tissue Stain. At higher magnification the elastic tissue of steerhide appears as shown in Fig. 5. As in the calfskin most of the elastic tissue is located in the region of the oil glands with little elastic tissue being present below the top of the sweat glands. The arteries present also have the elastic tissue as part of their walls.

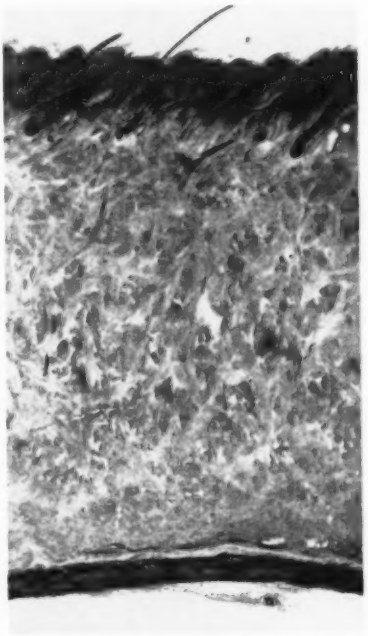

FIGURE 4.—Cross section of fresh steerhide stained with Weigert's Elastic Tissue Stain.

When a piece of fresh calfskin is placed in the autoclave for 4 hours at 15 pounds pressure, the collagen is digested, and the epidermis, its appendages, and the elastic tissue remain behind as a residue. A picture of such treated stock in cross section is shown in Fig. 6. The epidermis swells as a result of such treatment but still retains most of its original structure. The hair roots also are altered but still present. The elastic tissue tends to contract but is not greatly altered.

After the bating operation the residue remaining appears as a sheet of tissue as shown in Fig. 7. This tissue has been stained with Weigert's Elastic Tissue Stain; at this magnification the fibers are not easily identified, but under higher magnification the fibers can be seen. A stained cross section of the sheet shows the elastic tissue fibers to be present but not as receptive to the stain as obtained with the fresh skin in Fig. 6.

FIGURE 5.—Cross section of the epidermal area of fresh steerhide stained with Weigert's Elastic Tissue Stain.

FIGURE 6.—Cross section of the epidermal sheet remaining after being autoclaved for 4 hours at 15 pounds pressure and then stained with Weigert's Elastic Tissue Stain.

When a horizontal section is cut of the epidermal area of dyed and finished calfskin leather and the section decolorized and then stained with Weigert's Elastic Tissue Stain, the picture shown in Fig. 8 is obtained. The elastic

tissue has been reduced in amount, but broken fibers still remain. Examination of these fibers in the finished leather at high magnification shows them to be broken into a series of fine particles rather than as the continuous fibers which are seen in the fresh skin.

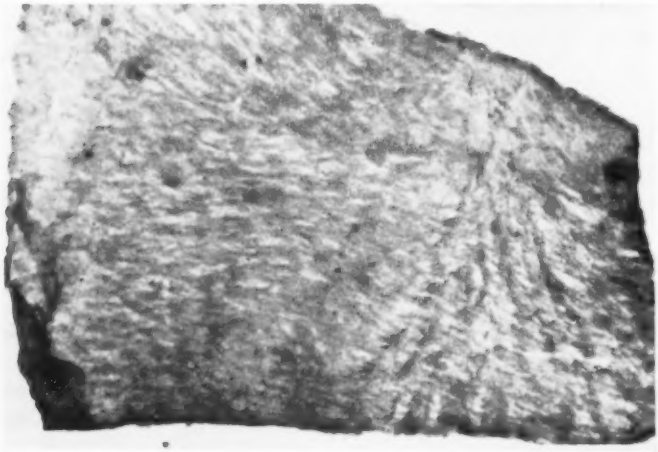

FIGURE 7.—Sheet of tissue of bated calfskin which had been autoclaved at 15 pounds pressure and then stained with Weigert's Elastic Tissue Stain.

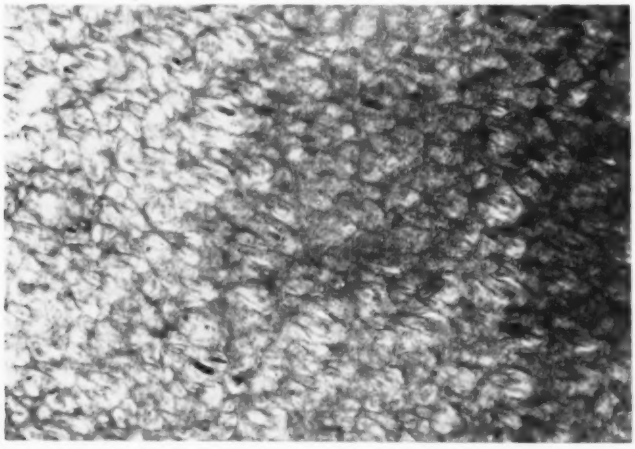

FIGURE 8.—Section cut in horizontal plane of calfskin leather stained with Weigert's Elastic Tissue Stain.

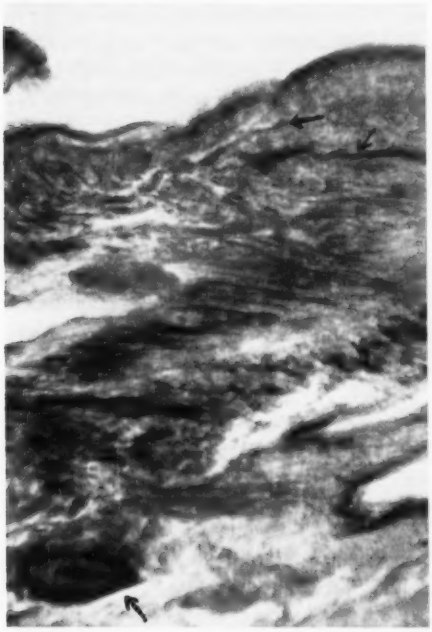

FIGURE 9.—Cross section of the epidermal area of chrome-tanned calfskin stained with Weigert's Elastic Tissue Stain.

In Fig. 9 the elastic tissue in the blood vessels in the epidermal area of chrome-tanned leather is shown. These are the smaller blood vessels near the grain surface and the larger blood vessel near the base of the hair roots which are readily traced by staining with Weigert's Elastic Tissue Stain.

The foregoing figures indicate that elastic tissue is altered by processing and that some of the tissue may be removed but that the residue is still very demonstrable. As indicated by the work of Tancous (6) and Stubbings (7) the normal beamhouse procedures remove practically all the nonfibrous proteins from skin. Hydrolysis of the collagen from the skin results in the fraction of elastin and hair-root debris. As the hair-root debris was reasonably uniform over the skins selected for the present work, the elastin could be calculated using two procedures developed. One procedure was for limed, unhaired skins, and the other procedure was for stock processed in the tannery to the "chrome in the blue" state. For the limed, unhaired stock the procedure selected has as a major feature the deliming of the residue, which is not necessary for the tanned stock as the results obtained from the two procedures will show.

LABORATORY PROCEDURES FOR DETERMINATION OF ELASTIN-KERATIN RESIDUE

Procedure I—(Elastin-keratin residue in limed and bated stock)

Preparation of lime stock.—Cured calfskin stock was fleshed and soaked in water for 16 hours at room temperature in the proportion of 4 parts of water to 1 of cured skin. A second soak in fresh water in the same proportions for

a period of 4 hours was then given. The skin was limed with straight lime solution for 7 days using a 4-to-1 ratio of water to cured-skin weight and 12% hydrated lime on the cured weight. The stock was then unhaired, scudded thoroughly, and fleshed. Blocks of 4 specimens, each specimen 2¾″ x 2¾″, were cut from over the whole skin to furnish 3 test lots and one control lot.

Removal of elastin.—The stock was surface-delimed with hydrochloric acid, then completely delimed with boric acid at 75°F. Controlled conditions were established using large bottles immersed in a bath at 75°F. and rotating at 45 rpm. Then 1% $NaHCO_3$ on the white weight was added, and the temperature was raised to 90°F. The elastin-removing enzyme (powder* from a whole raw pancreas, activated, desiccated, and defatted) was added, and bating was continued for the required time. The squares were then blotted on towels, wrapped in wax paper and aluminum foil, and placed in a freezer to stop enzyme action.

Digestion of soluble hide components.—After being defrosted the specimen squares were individually pressed in a Carver press at 10,000 pounds ram pressure to remove most of the water. They were then dried overnight in a vacuum oven at 80°C. and 22 inches of mercury, cooled in a desiccator, and weighed.

The dried squares were placed in separate 400-ml. beakers, and sufficient distilled water was added to yield approximately a 3% gelatin solution. The beakers were covered and placed in an autoclave for 4 hours at 15 pounds steam pressure. After this the hot solutions were decanted through previously dried and weighed coarse-fritted glass crucibles. The residues in the beakers were treated with hot 0.5*N* HCl to remove calcium, then transferred to the crucibles with hot water. The crucibles were then washed alternately with hot acid and hot water until all lime and acid were removed from the residues.

The washed crucibles were placed in Soxhlet equipment, and the grease in the residues was removed by extraction with acetone for 4 hours. The crucibles were then air-dried and finally placed in a desiccator overnight to dry to constant weight. The percent residue of the dried squares was calculated. Comparison of the percent residues of treated lots with that of the control gave a measurement of degree of removal of elastin.

Procedure II—(Elastin-keratin residue in leather in the blue)

Twenty-seven specimen squares were cut from matching positions from right and left sides of the three skins being examined. After being blotted with filter paper each square was weighed to establish reference weights and then placed in Petri dishes. Fifty ml. of distilled water was added to each dish, and the dishes containing the specimens were placed in an autoclave

*Viokase powder P-145-D, produced by the Viobin Corporation, Monticello, Ill.

for 4 hours at 15 pounds steam pressure. The dishes were then removed from the autoclave, the solutions were poured off the specimens, and the specimens were washed in distilled water and then soaked in water overnight.

After soaking in water overnight the specimens were blotted with filter paper to a condition where they no longer showed a water mark on the filter paper. The specimens were then weighed, and the percent elastic-tissue residue was calculated.

A portion of each residue after soaking overnight was stained with Weigert's Elastic Tissue Stain to demonstrate the elastic tissue in the residue. This demonstrated both the elastic tissue in the basketlike network of the epidermal area and the elastic tissue in the arteries.

EXPERIMENTAL RESULTS

Table I shows illustrative data obtained from two limed calfskins.

TABLE I

PERCENT ELASTIC TISSUE AND KERATIN REMAINING IN CALFSKIN AFTER BATING

(Average of 20 values)

	1st Skin		2nd Skin	
	Control	0.01% Enzyme	Control	0.03% Enzyme
Percent residue	2.21	1.55	2.78	0.38
Standard deviation	0.41	0.33	0.43	0.11
Percent decrease in residue		30		86

Examination of the values for the percent residue in the two calfskins before bating, listed as controls in Table I, shows that the first calfskin contains less elastic tissue then the second calfskin. When portions of the two bated calfskin residues were stained and examined microscopically, the elastic tissue in the residues was still present but broken into fragments rather than as a continuous sheet. There was very little residue from the calfskin specimens treated with the 0.03% enzyme.

Although the standard deviations are fairly high, representing as they do the differences in blocks over the whole skin and including effects of thickness differences and possibly keratin residue differences in addition to experimental error, statistically they permit a 95% assurance that even an 11% decrease in residue would have significance for the first skin and 8% for the second skin.

In Table II the data obtained from the analysis of the three skins in the blue are arranged to show symmetry between sides, differences between rows parallel to the backbone, and a comparison between the skins. The stained

residues from each calfskin were examined microscopically, and it was observed that the arteries were similar in distribution and size on each side of the calfskins. The veiny calfskins showed more pronounced and less diffuse arteries present in the residues than those observed in the non-veiny calfskin.

It is obvious that the veiny leather has more elastic tissue residue than the normal leather. Although a somewhat less precise technique was used in obtaining the values shown than in the case of the limed skins, it is informative to know that such a rapid method can be used to produce useful results.

TABLE II

PERCENT ELASTIC TISSUE AND KERATIN IN NON-VEINY AND VEINY CALFSKIN LEATHER

(Average of 27 values per side)

	Non-Veiny Skin		Veiny Skin No. 1		Veiny Skin No. 2	
	Left Side	Right Side	Left Side	Right Side	Left Side	Right Side
Percent residue	1.91	2.19	2.74	2.79	2.77	2.94
Standard deviation	0.25	0.18	0.27	0.27	0.25	0.34

CONCLUSIONS

By microscopic examination of cross sections stained with an elastic-tissue stain and by the two methods developed for isolating the elastic-tissue residue of animal skin it is possible to determine the influence of processing operations on the elastic tissue. In regular calfskin processing there is a reduction in the amount of elastic tissue from that found in salt-cured calfskin.

When sufficient enzyme specific for breaking down elastic tissue is used, it is possible to remove almost all of the elastic tissue from the skin or hide. In the present work under the test conditions used it was possible to remove 30% and 86% of the elastic tissue in the bating operation by using an enzyme powder from whole raw pancreas, which was activated, desiccated, and defatted.

A comparison of non-veiny and veiny calfskins showed that the veiny calfskins contained more elastic tissue. The comparison made also established that there are similar amounts of the elastic tissue on each side of the calfskin, showing that symmetry occurs between sides of a given skin.

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DISCUSSION

DR. EDWARD F. MELLON (Eastern Regional Research Laboratory): We are indebted to Mr. Roddy for an excellent demonstration of the ability of histological techniques and chemical determinations to show us the location of elastic tissue and the amount of elastic tissue present in a hide.

An observation which we had made at the time we demonstrated the elastic-tissue network in the hide confirms very well the histological demonstration which you saw this morning of a high concentration of elastic tissue around the hair follicle and just about midway down the depth of the grain layer.

The slices which we had cut, which were about one-tenth of a millimeter thick, at the grain surface did not show any large concentration right at the hair follicle. But as we reached this medium depth of the grain layer the concentration of elastin was so great that in these small slices you could actually see a bump where the hair follicles were. There was a bump, a ridge around the outside, and the hole where the hair shaft had gone through it. I think this is very good confirmation of the histological pictures which we saw today.

I have one question: In the breakdown of these fibers which we have noted, after you have treated the hide under certain conditions, would you say that this breakdown of the fibers is something that might be progressive? Do you dissolve the outside of the fibers, making them smaller until they finally break through, or do you break off a chunk and leave the middle of the fibers?

MR. RODDY: That is a very nice question.

There has been information and literature in recent years that in staining elastic tissue what you are really doing is staining perhaps a mucoid fraction surrounding the individual elastic-tissue fiber. Some years ago when we worked with the neck ligament and cut it in cross section, the fibers in cross section were stained completely with the Weigert's Elastic Tissue Stain.

Now the question brought up by Dr. Mellon was: Is this elastic tissue gradually broken down? It definitely is. As an example, if we leave it in the autoclave for a period of 6 to 8 hours, we will dissolve much more elastic tissue than if we leave it in for the 2 to 4 hours that we selected in the present work. So there definitely is a breakdown. However, the point I tried to

make in the course of my talk is that the elastic tissue during the course of ordinary tanning is still present in the finished leather and still demonstrable by Weigert's Elastic Tissue Stain; and also we can recover this elastic-tissue residue from calfskin as shown in the case of the chrome stock where we recovered as much as 2% from the non-veiny skin and 2.75% to almost 3% in the case of the veiny skins.

DR. SELIGSBERGER (Quartermaster Research and Engineering Center): Do I understand you right, that keratin is included in the figures in the table? And how much keratin is actually present?

MR. RODDY: I mentioned in the course of the talk, Dr. Seligsberger, that Dr. Stubbings tried to remove this hair-root keratin from the elastic-tissue fraction and in the course of doing that he was able, using strong sulfide, to remove the keratinous material, but he also reduced the elastic tissue. Tancous, in her work, showed the elastic-tissue fraction was 2.2%. On the other hand, the work by Dr. Mellon and coworkers showed that the elastic tissue as a residue based on total nitrogen was somewhere in the neighborhood of 2%. So the elastic-tissue residue is somewhere in that particular region, and the small amount of keratin you would have as a hair-root debris, which is not removed by standard processing, would only be a very small amount apparently.

MILTON BAILEY (U. S. Navy Research & Development Facility): We have had some rather interesting experience with calfskin versus stuffed side leathers so far as water-resistance deterioration is concerned. We found that stuffed leathers would crack across the vamps very rapidly, whereas our calfskin withstood this kind of wear for considerable periods of time. I wonder if the elastic tissue is a major factor in causing this kind of resistance as far as calfskin is concerned.

MR. RODDY: We do not have that information as yet. However, at the present time at Cincinnati we are processing both side upper leather and calfskin leathers to determine exactly what influence this elastic-tissue removal will have upon the finished leathers.

DR. H. B. MERRILL (B. D. Eisendrath Tanning Co.): It seems very remarkable that according to what Mr. Roddy has said, the autoclaving process actually destroys collagen even when it is chrome-tanned, without affecting the elastin. Is that correct, Mr. Roddy?

MR. RODDY: It removes both the collagen and also the chrome-tanning material. The process when used on vegetable-tanned leather will also dissolve the collagen, but the difficulty you run into is that you get polymeriza-

tion of the vegetable tanning materials with the breakdown in the collagen, and, of course, the elastic-tissue residue becomes much harder to separate. I might also point out at this time that if we take fresh skin or hide and use this autoclaving technique, it is possible to remove the collagen and leave the epidermis (reasonably intact with slight swelling of the epidermal cells), the hair, the oil glands, and the elastic tissue as a residue.

Dr. Joseph Naghski (Eastern Utilization Research & Development Division): Workers at the American Meat Institute Foundation found when they studied the elastic tissue in meat that the enzymes digested out the center portion of the elastin fibers leaving a ghostlike shell. Did you observe anything like that in the skin tissue as contrasted with the meat?

Mr. Roddy: No, we did not. I brought up the point a while ago that when we took the ligament and cut it into cross section we did not come up with the shell-like idea. You can stain the fiber completely through even in the case of finished leather.

Dr. Andrew Salamatov (Barrett & Co. Inc.): I would like to pursue the sulfide a little further. You said strong sulfide removes 15%. What is meant by "strong"?

The second part of my question is: If it dissolves 15% of skin, what happens to the rest of it? Maybe it is broken down by sulfide treatment.

Mr. Roddy: The work which I was quoting was that of Dr. Stubbings, and of course, he was removing the keratin residue from the elastic tissue which he had isolated, and that is where the 15% breakdown of keratin occurred.

It is possible, as an example (I mentioned it previously), just by water to ultimately digest the elastic tissue. Therefore acid or alkali will also break it down. The point that is made is this: It happens to be apparently much more resistant tissue in an aqueous system than the collagen, and therefore you can make a separation in a manner in which we have done—from fresh skin all the way through processing and on tanned stock. The only exception which I mentioned was in the case of the vegetable-tanned stock. We had difficulty there. On the other hand, with care and proper removal of the water from the stock during the course of autoclaving, it is also possible to obtain a residue from vegetable-tanned stock. It is a little more tedious to do, but it can also be obtained.

Dr. Harold G. Turley (Rohm & Haas): I do hope the impression is not given by the speakers here that all this work was original. I suppose 35 years ago it was a controversial question in this Association. I do hope that due

credit will be given to Dr. John Arthur Wilson for the demonstration of elastin and the way it behaved in tannery treatments, and also to Dr. Hollander who proved at that time in practical leathermaking that elastin is broken down and not necessarily removed.

However, I do find interesting and original this demonstration of the greater amount of elastin in veiny hides. But I would like you to show, in connection with the technique, that there is some correction applied there with regard to residues. I am wondering if you have done any work with pure isolated elastin itself, putting it through the different techniques, and whether you have some idea of the recovery.

MR. RODDY: We are giving full recognition to the work done by John Arthur Wilson, Hollander, and previous investigators.

Our major issue here, of course, is to show that it is possible by chemical analysis or a chemical technique to isolate the elastic tissue.

I appreciate, as you do, Dr. Turley, the work that has gone on before, not only by John Arthur Wilson, but also by Dr. Merrill who is in the audience, and who has used a similar technique for enzyme removal of the elastic tissue of calfskin, and I would like to go on record to say that is the case.

In regard to using the pure elastic tissue, some years back when we presented information on using the elastic tissue as a biological source from the neck ligament, it was argued as to whether it would resemble the elastic tissue in animal skin.

I might point out that in the course of doing this work in Cincinnati we had a man by the name of Earl Chia, from Formosa, visit our laboratory. Upon seeing the elastic tissue removed from skin and hide, and the ligament put into the autoclave for digestion purposes, he was very curious. I explained what we were doing. And of course he predates anyone else from the standpoint of the record of using a technique of this nature. He says that it was handed down in his family for generations. The pressure cooker was used to digest ligament and collagen to break it down to protein of a soluble nature and the right size so that it could be ingested by the family. So it predates everything.

As I say, then, Dr. Turley, I would like to give recognition to the gentlemen mentioned and to anyone else who has been concerned with this type of work.

A recent survey by the Manufacturing Chemists' Association indicated that nearly 50% of its member companies are engaged in, or directly interested in, foreign operations. It is estimated that some 15% of the 1959 capital outlay by U.S. chemical firms will be or has been for plants and facilities abroad.

WATER PENETRATION TESTING MACHINE FOR SOLE LEATHER

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ABSTRACT

A test to measure the water resistance of sole leather has been developed. A leather specimen is flexed at a frequency of 30 cycles per minute with one side exposed to water until penetration occurs. The specimen is clamped so that the angle of bend is approximately 90°. The results show that flexing increases the rate of water absorption as well as the rate of water penetration compared to the rates under static conditions. Studies were made on the influence of thickness of specimen, location on the sole leather bend, and compression of the specimen on dynamic water penetration and water absorption. The logarithm of the number of flexes required for penetration is a direct function of the thickness of the leather. The rates of water penetration and water absorption depend on the location of the specimen on the sole leather bend. Compression of the impregnated leather decreases the rate of water penetration and the rate of water absorption.

INTRODUCTION

The flexural properties of leather and its ability to transmit water vapor make it a highly desirable material for the construction of shoes. However, its porosity causes weak resistance to liquid water penetration and treatments must be applied to improve its properties in this respect. This investigation is concerned with a method by which the resistance of leather to water penetration can be measured under simulated conditions of practical wear, and with some factors that affect the rate of water penetration.

A number of test methods (1) based on the application of water under pressure and static conditions have been used to determine the water resistance of leather. These methods, as pointed out by Weir, Carter, Newman, and Kanagy (2), do not give a reliable measure of water resistance under conditions of use, since leather in use is subjected to flexing conditions that influence water penetration. It has been established that penetration of water through the leather under dynamic conditions involves a complicated

mechanism. It is assumed that water penetrates by means of a force introduced by fiber stresses as the leather is flexed. Mitton and Hyde (3) have indicated that one would encounter great difficulty in attempting to derive a mathematical formulation for the penetration process. It was pointed out, however, that thickness and density of the leather are properties related to the process.

In this investigation, the water penetration resistance of leather was measured by means of a machine that flexes the leather in the presence of water. The resistance to penetration was evaluated in terms of the number of flexes and/or the time required for penetration.

APPARATUS AND PROCEDURE

The apparatus consists of reciprocating jaws for flexing the specimen, a tube to apply water to the underside of the specimen, and an electronic device for turning off the machine when the water penetrates. The machine is shown in Fig. 1. A top view diagram with some dimensions is shown in Fig. 2. A cross-sectional diagram showing over-all dimensions and the positions of a leather specimen in both the unflexed (J_1) and flexed (J_2) positions is presented in Fig. 3.

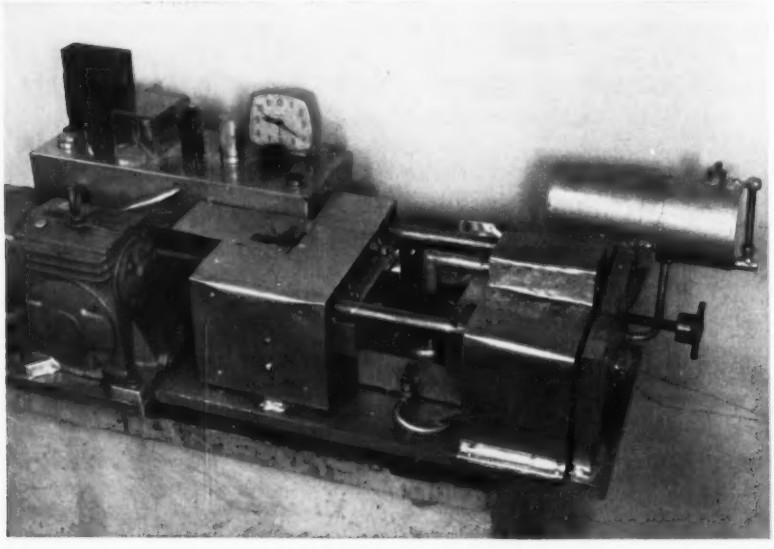

FIGURE 1.—Water penetration machine.

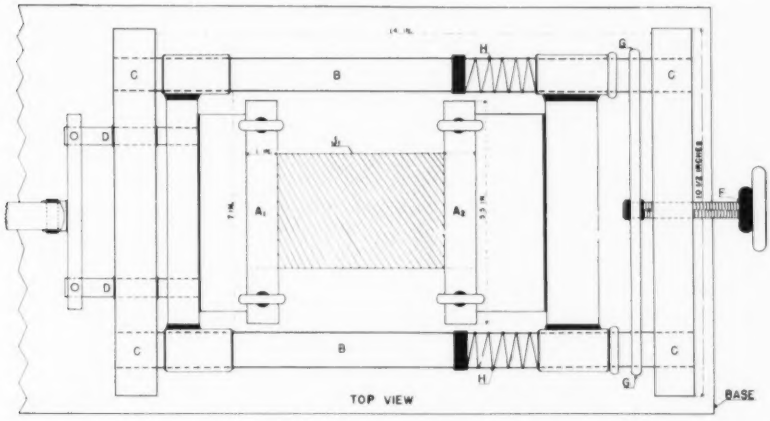

FIGURE 2.—Top view of water penetration machine with some dimensions.
A_1 and A_2—Jaw assemblies
B—Support and tracks for jaw assemblies
C—End panels
D—Coupling to motor
F and *G*—Setscrew and jaw spacer bar
H—Compression spring
J_1—Unflexed specimen

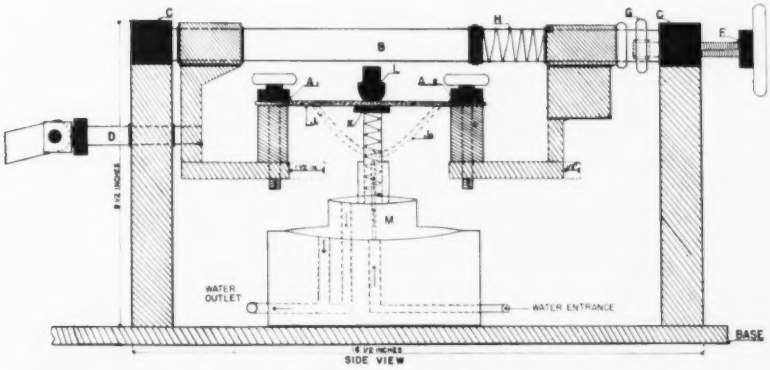

FIGURE 3.—Cross-sectional view with some dimensions of water penetration machine.
A_1 and A_2—Jaw assemblies
B—Support and tracks for jaw assemblies
C—End panels
D—Coupling to motor
F and *G*—Setscrew and jaw spacer bar
H—Compression spring
J_1 and J_2—Specimen unflexed and flexed
K—Lower terminal wetting device
L—Top terminal
M—Water container

The flexing mechanism consists of two movable jaw assemblies, one of which (A_1) is operated through couplings (D) that are journaled in cylindrical bearings mounted in the mid-portion of the end panels (C). This assembly is reciprocated by a ratiomotor geared at 30 cycles per minute; its maximum displacement is approximately 1.5″. The displacement of the other jaw (A_2) varies within the limits of 0.0″ to 0.5″; it is actuated by the specimen only to the extent necessary to control tension during the operation. A spring (H) also aids in the control of the motion of this jaw. The assemblies extend approximately 8″ across the machine. Bearings, integrally mounted in the top section of the assemblies, are mounted so they may slide on 1″ x 16″ steel tracts (B) which serve as supports and guides for the jaws. The outboard ends of the tracts pass through bores in the top section of 1″ x 7″ x 10″ steel end panels (C) and are detachably secured thereto by screws. The end panels are welded to the base of the machine. The separation of the jaws is controlled by a setscrew (F) and a spacer bar (G).

It can be seen that the specimen is flexed so that the crease is perpendicular to the longitudinal axis of the machine and the convex surface is below the plane of the applied force. The original shape of the specimen is not fully restored when the jaws return to their original positions due to the viscosity of the leather and to the pressure applied by the top terminal (L).

The wetting device (K) is a pump-type plunger suspended vertically by a spring in the neck of a water-filled container (M) and maintained in contact with the specimen at every stage of the cycle. The bottom end of the plunger is open and the top end is covered with a circular perforated metal plate about $\frac{3}{4}$″ in diameter. The plate is countersunk at the center to retain water momentarily and bevelled at the edge to prevent too severe scuffing of the specimen. On bending, the specimen forces the plunger downward into the water; a pumping action results from the reciprocal motion. Water entering through the bottom end of the plunger is forced up and through the perforations in the top plate, thus producing a spray on the surface of the specimen. The water is forced out in spurts rather than as a continuous flow. As a result of the constant contact with the specimen, the lower plunger serves as a mild abrader as well as a terminal in the electrical circuit. The plunger tends to rotate to a certain degree as the specimen is unbent in the cycle, thereby giving an abrasive effect that simulates conditions to which the sole of a shoe is subjected when worn.

The top terminal (L) is curved to conform with the crease formed in the bent specimen and is held against the surface of the specimen by a spring (*see* Fig. 4A). A segment of this foot extends vertically and fits loosely into a metal housing which permits a to-and-fro motion of the foot. This motion is dependent upon the resilient action of the spring and corresponds to a rocking angle of about ±15°. The rocking has the advantage that penetration points surrounding the foot may be detected as well as those occurring

in the center of the crease. Penetration is found to occur over a greater area for non-impregnated specimens than for impregnated specimens.

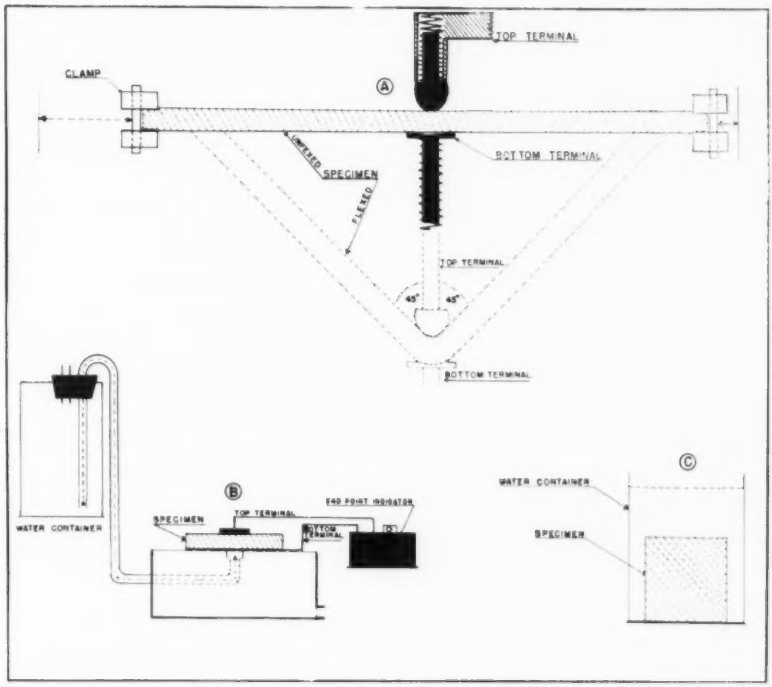

FIGURE 4.

A—Dynamic water penetration test
B—Static water penetration test
C—Static immersion water absorption test

Specimens having various widths, or a half sole of conventional width, can be tested on the machine. Sizes under 2½″ in width were found to be unsatisfactory because water frequently escapes around the edges and makes contact with the top terminal, especially when the resistance of the specimen to penetration is very great. To clamp the specimen on the machine, the jaws are set about 4½″ apart; therefore, the specimens should have a minimum length of 6″ to assure proper clamping. A jaw separation of 4½″ produces an angle of bend of approximately 90°, as illustrated in Fig. 4A.

The conditions for testing depend upon the stiffness and thickness of the leather. Finished sole leather cracks on bending with greater ease than unfinished leather; therefore, the former is used to determine the angle of bend for the different types of leather to be tested.

The flexing mechanism of the machine is provided with a compression spring (*H*) (*see* Figs. 2 and 3) which compensates for possible changes in stiffness and thickness of the specimen that may occur during the flexing cycles.

MATERIALS AND SPECIMENS

Commercial sole leather was used in this investigation. A group of specimens prepared at the Virginia Oak Tannery included non-impregnated vegetable-tanned crust, impregnated vegetable-tanned crust, and non-impregnated vegetable-tanned finished leather. The impregnated specimens were prepared by the Votan process*. Impregnated specimens of vegetable-tanned crust leather were also prepared in the NBS leather laboratory using a blend of a low-molecular-weight polybutene† and a resin prepared by the polymerization of rosin‡.

Specimens used for the water penetration tests on the machine were 3″ x 6″. Specimens 2″ x 2″ for the static tests (*see* Fig. 4, Methods B and C) were cut from the non-dampened parts of the specimens used in the dynamic (flexing) test. All specimens were conditioned in an atmosphere at 23°± 1°C. and 50% relative humidity prior to testing.

RESULTS AND DISCUSSION

Figure 4 shows the different methods employed for measuring the water resistance of the leathers. In Method A the specimen is flexed repeatedly through an angle of approximately 90°. Water is applied to the under-surface by means of a tube which also acts as a terminal, and penetration is detected when the water makes contact with the top terminal. In Method B the water is applied to the under surface of a stationary specimen by means of a tube. The rate of flow is controlled to about 4 to 5 ml. per minute. The end point is detected by an electronic device as in Method A. Method C measures the amount of water absorbed by immersion of the specimen under static conditions. The specimen is removed from the water after a specified immersion period, weighed, and the percentage increase in weight is calculated.

INFLUENCE OF FLEXING

Using Method A above, the effects of flexing on the rate of water penetration and water absorption were studied with various types of sole leather.

*Votan is a blend of a resin prepared by the polymerization of rosin (Polypale, Hercules Powder Company) and a copolymer of isobutylene and isoprene (Butyl rubber, Standard Oil Company of N. J.).
†Oronite, Oronite Chemical Company.
‡Polypale, Hercules Powder Company.

Water was applied to the grain side only of all specimens except those of the finished leather which were also tested with the application of water to the flesh side. The results are given in Table I.

TABLE I

RESISTANCE TO WATER PENETRATION UNDER DYNAMIC AND STATIC CONDITIONS

Type of Leather	Penetration Time*		Water Absorbed at the Time of Penetration†	
	Flexed	Unflexed	Flexed	Unflexed
	min.	*min.*	*g.*	*g.*
Non-impregnated vegetable-tanned crust	14.2 ± 0.7	36 ± 8	2.7 ± 0.3	1.3 ± 0.1
Chrome-retanned crust	6.2 ± 0.5	16 ± 2	2.0 ± 0.3	0.7 ± 0.1
Vegetable-tanned finished (water applied to grain side)	271 ± 42	413 ± 49	2.1 ± 0.2	2.8 ± 0.3
Vegetable-tanned finished (water applied to flesh side)	171 ± 35	254 ± 34	8.5 ± 1.3	5.7 ± 1.2
Impregnated vegetable-tanned	470 ± 150	1680‡	2.5 ± 0.6	1.7**

*Geometric averages for 7 specimens tested (*see* text); the numbers following the ± sign are the standard errors of the averages.
†Arithmetic averages for 7 specimens tested (*see* text); the numbers following the ± sign are the standard errors of the averages.
‡Single specimen discontinued without penetration.
**Water absorbed at the time the test was stopped.

It will be noted that for time of penetration in this table and for the number of flexes in subsequent tables the results are reported as geometric averages rather than as arithmetic averages. The reason for this treatment of the data lies in the fact that the time of penetration and number of flexes to penetration have skew distributions in which values considerably larger than the average are much more likely to occur than correspondingly low values. Furthermore, the scatter of the values obtained for replicate specimens increases rapidly with the magnitude of the measurement. Data of this type are best transformed into logarithms prior to statistical analysis. The logarithm scale compresses the region of very large values, thus reducing the preponderant effect of abnormally large values and eliminates to a large extent the dependence of the scatter on the magnitude of the measurement. If an average is calculated on the logarithms of the individual measurements and then transformed back into the original scale, the result is a geometric average of the original measurements. For the reasons outlined above such a geometric average is a more cogent measure than an ordinary arithmetic mean. The standard errors listed in all tables are the standard deviations of replicate measurements divided by the square root of the number of replicates.

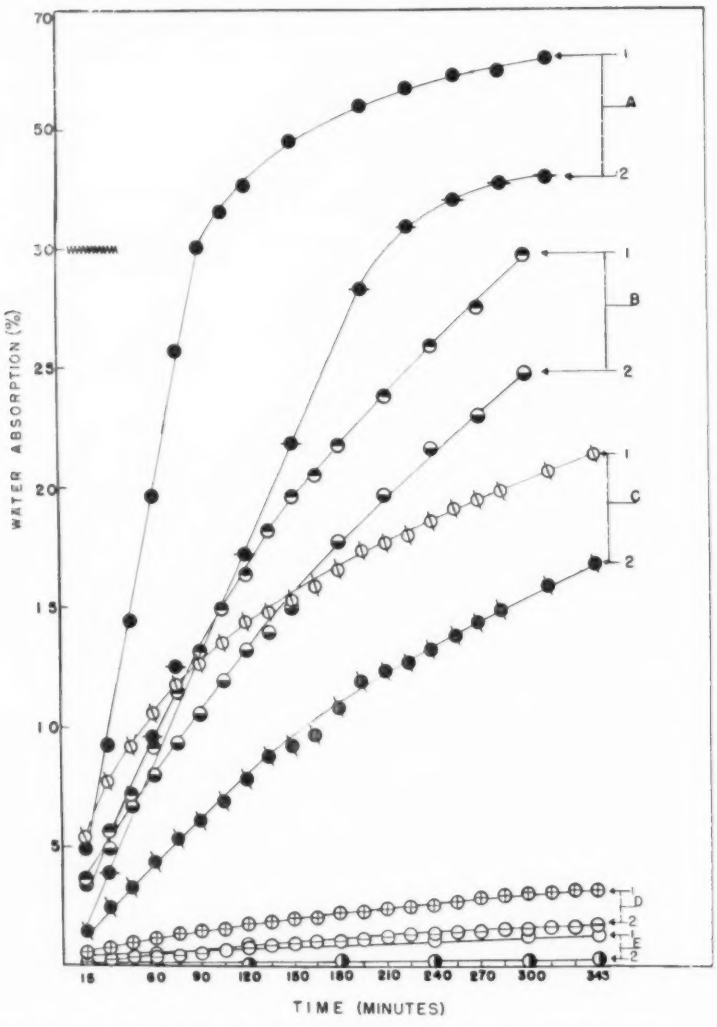

FIGURE 5.—Rate of water absorption for specimens in water penetration tests.
1—Flexed 2—Unflexed
A—Chrome-retanned crust leather
B—Non-impregnated vegetable-tanned crust leather
C—Non-impregnated vegetable-tanned finished leather (water applied to flesh side)
D—Non-impregnated vegetable-tanned finished leather (water applied to grain side)
E—Impregnated vegetable-tanned crust leather

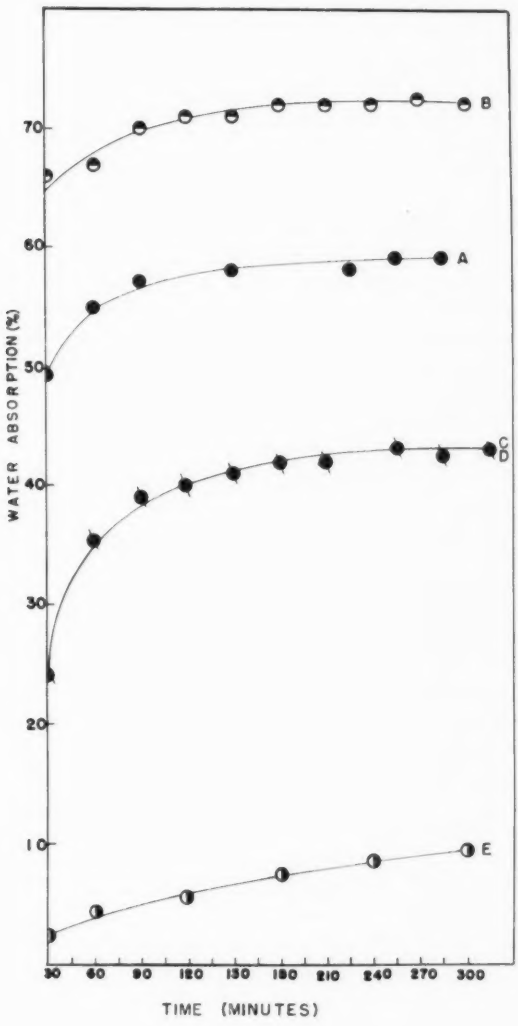

FIGURE 6.—Rate of water absorption for specimens immersed in water.

B—Non-impregnated vegetable-tanned crust leather
A—Chrome-retanned crust leather
CD—Non-impregnated vegetable-tanned finished leather
E—Impregnated vegetable-tanned crust leather

The results in Table I indicate that flexing increases the rates of water penetration and water absorption of the specimens. Weir, Carter, Newman, and Kanagy (2) have indicated that flexing the leather causes a pumping action which is partly responsible for the rapid penetration. In this test it was observed that the water appears to enter the voids of the leather as the specimen is bent and is forced through the voids as the specimen is unbent. Penetration is generally detected during the return of the moving jaw to its original position.

The results show differences in water penetration resistance caused by different treatments, tannage, and also difference in resistance of the grain and flesh sides of the finished leather. The resistance is lowest for the chrome-retanned crust and highest for the impregnated vegetable-tanned crust leather. In comparing the resistance of the flesh side with that of the grain side of the finished leather it will be seen that the grain side is more resistant to water penetration and to water absorption.

The behavior of these leathers with respect to water absorption is shown in Figs. 5 and 6 in which the percent of water absorbed is plotted against the time of exposure in minutes. Each curve is obtained from measurements on a single specimen. Unfortunately, these curves are incomplete due to the great amount of time required for the specimens to come to equilibrium. The curves shown in Fig. 5 are typical water absorption curves for the flexed and unflexed water-penetration specimens, respectively. The results obtained by Methods A and B of Fig. 4 show the increase in the amount of water absorbed by the flexed specimen (1 in Fig. 5) in comparison with that absorbed by the unflexed specimen (2 in Fig. 5). It will be noticed that the rate of absorption is greatest for the chrome-retanned leather (*A*). The improvement in water resistance due to impregnation is reflected by the differences between the amounts of water absorbed by the impregnated leather (*E*) and the non-impregnated vegetable-tanned crust leather (*B*). The rate of absorption of the non-impregnated vegetable-tanned finished leather is considerably greater when the water is applied to the flesh side (*C*) rather than the grain side (*D*). Since the grain contains relatively smaller pores and is less spongelike in form than the flesh side, it is to be expected that its resistance to water absorption will be greater.

The results given in Fig. 6 were obtained with 2″ x 2″ specimens tested by Method *C*, Fig. 4. This method is similar to the static water absorption test, KK-L-311a, Method 8111. The results show that the behavior of these specimens with respect to water absorption is similar to that of the specimens tested by Methods A and B, Fig. 4, in which only a small portion of the specimen was exposed to the water. However, in comparing the results obtained on a 30-minute basis, it can be seen that the rate of absorption is greatest for the specimens immersed in the water. It may also be noted that under each set of testing conditions the leathers rank in the same relative

TABLE II

EFFECT OF BEND LOCATION ON WATER PENETRATION UNDER DYNAMIC CONDITIONS* OF VEGETABLE-TANNED LEATHER GIVEN VARIOUS TREATMENTS

Location on bend†	Number of Flexes before Penetration‡			Water Absorption at Time of Penetration**			Chloroform Extract**††	
	Non-impregnated crust	Finished	Impregnated crust‡‡	Non-impregnated crust	Finished	Impregnated	Finished	Impregnated crust
				g.	g.	g.	%	%
A	490 ± 60	3400 ± 900	6500 ± 1700	1.7 ± 0.2	2.0 ± 0.2	1.2 ± 0.2	4.5 ± 0.5	19.1 ± 3.5
B	240 ± 60	1500 ± 500	4700 ± 1400	1.8 ± 0.3	2.1 ± 0.3	1.2 ± 0.3	3.8 ± 0.6	21.3 ± 0.5
J	210 ± 24	2700 ± 350	5700 ± 1400	1.4 ± 0.1	1.7 ± 0.2	0.9 ± 0.1	4.0 ± 0.3	19.0 ± 1.2

*Thirty flexes per minute.
†A—Butt area; B—Shoulder area; J—Belly area.
‡Geometric averages for 7 specimens tested (*see* text); the numbers following the ± sign are the standard errors of the averages.
**Arithmetic average value for 7 specimens taken from 7 different bends; the numbers following the ± sign are the standard errors of the averages.
††A composite sample of the non-impregnated vegetable-tanned crust leather contained 3.5% grease.
‡‡Impregnated at Virginia Oak Tannery.

positions except that the chrome-retanned leather (Fig. 6, *A*) is lower in order than the vegetable-tanned crust leather (*B*). The vegetable-tanned finished leather (*CD*) is so identified since the water was applied both to the grain side and to the flesh side in test Methods A and B of Fig. 4.

INFLUENCE OF THICKNESS

The effect of thickness on the rate of water penetration was studied with non-impregnated vegetable-tanned finished leather. The specimens were tested under dynamic conditions with the water applied to the grain side. The thickness of the specimens was varied by splitting successive layers from the flesh side. The results of the test are shown in Fig. 7, in which the loga-

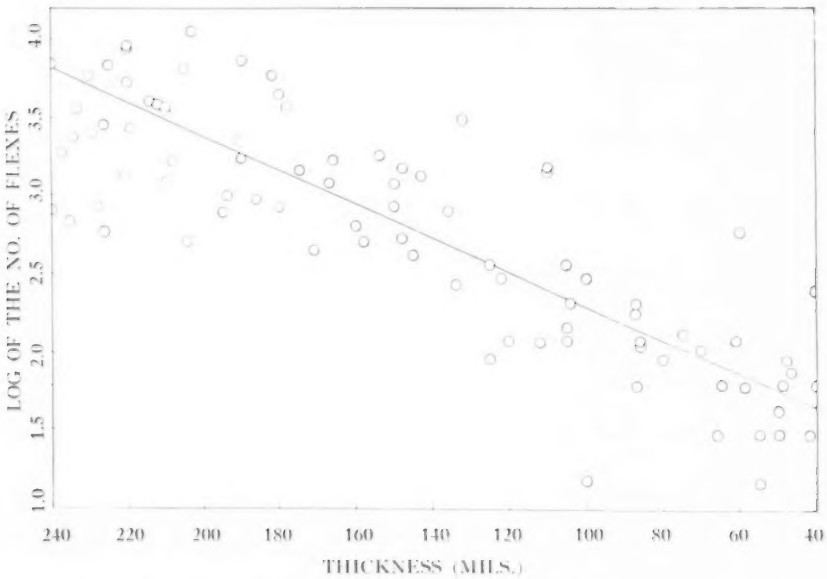

FIGURE 7.—Relation of thickness of leather and number of flexes before water penetration.

rithm of the number of flexes before penetration is plotted against thickness in mils. A straight line is drawn through the points to indicate the trend of the data. The results show that the logarithm of the number of flexes is related to the thickness of the leather in an essentially linear way.

INFLUENCE OF LOCATION

For this study specimens were sampled in accordance with the Official Methods of the American Leather Chemists Association (4). The results of the tests to determine the effect of location on the sole leather bend on water penetration and water absorption under flexing conditions are given in Tables II and III. In all cases the average of the number of flexes required for penetration is largest in the butt area (location *A*). On the other hand, the differences in these averages between the shoulder area (location *B*) and the belly area (location *J*) are mostly small and show no consistency for the various leathers examined.

TABLE III

EFFECT OF BEND LOCATION ON WATER PENETRATION UNDER DYNAMIC CONDITIONS* OF VEGETABLE-TANNED LEATHER NON-IMPREGNATED AND IMPREGNATED AT NBS

Location on bend†	Number of Flexes before Penetration‡		Water Absorption at Time of Penetration**		Chloroform Extract**	
	Non-impregnated	Impregnated	Non-impregnated	Impregnated	Non-impregnated	Impregnated
			g.	g.	%	%
A	400 ± 50	5900 ± 140	3.0 ± 0.3	1.8 ± 0.2	3.9 ± 0.4	22.3 ± 0.4
B	190 ± 60	3000 ± 140	6.0 ± 1.6	1.6 ± 0.1	4.4 ± 0.6	23.4 ± 0.3
J	190 ± 20	4400 ± 100	3.9 ± 0.6	1.6 ± 0.3	4.2 ± 0.5	25.6 ± 1.6

*Thirty flexes per minute.
†A—Butt area; B—Shoulder area; J—Belly area.
‡Geometric average value for 5 specimens from a single bend; the numbers following the ± sign are the standard errors of the averages.
**Arithmetic average value of 10 specimens representing 5 sublocations on each of two bends; the numbers following the ± sign are the standard errors of the averages.

The amount of water absorbed is nearly the same for all bend locations on a given type of leather as shown in Tables II and III. This indicates that it is generally necessary for a definite amount of water to be present in the leather before penetration occurs. The rate at which this amount of water is absorbed is apparently a function of the water penetration resistance, as indicated by the number of flexes required in the different locations to obtain penetration.

In comparing the water resistance of the impregnated crust leather prepared at the Virginia Oak Tannery with that of the impregnated leather prepared in the NBS laboratory, it can be seen that the resistance of the former appears to be greater, even at the lower impregnant content.

The average value for grease content in any location of the non-impregnated vegetable-tanned crust leathers was less than 5%; therefore, the water

resistance of this leather was probably not influenced appreciably by the grease. Work by Kanagy and Vickers (5) has shown that degreasing had little effect on the water vapor transmission of the leathers when the grease contents were below a 5% level.

INFLUENCE OF COMPRESSION

For the work on compression impregnated specimens were prepared in sets of two; one was used as the control specimen, and the other was compressed for 5 minutes at 4000 lb/sq. inch. The resistance to water penetration was measured under dynamic conditions. The results, given in Table IV, show

TABLE IV

EFFECT OF COMPRESSION ON WATER RESISTANCE OF IMPREGNATED VEGETABLE-TANNED LEATHER UNDER DYNAMIC CONDITIONS

Non-compressed Leather			Compressed Leather	
Number of Flexes before Penetration*	Water Absorption at Time of Penetration†	Compression	Number of Flexes before Penetration*	Water Absorption at Time of Penetration†
	g.	%		g.
760 ± 100	3.2 ± 0.7	8.5	6900 ± 1200	2.8 ± 0.4

*Geometric average for 12 specimens tested (*see* text); the numbers following the ± sign are the standard errors of the averages.
†Arithmetic average for 12 specimens tested; the numbers following the ± sign are the standard errors of the averages.

that compression of the leather decreases both the rate of penetration and the rate of absorption; this is further evidence that the rates of penetration and absorption are functions of the porosity of the leather.

CONCLUSION

A machine has been developed for testing the water resistance of sole leather under dynamic conditions. The machine may be used to determine differences in water resistance caused by thickness, bend location, tannage, impregnating materials, and compression of the leather. The test should be useful in the development of improved impregnants to increase the waterproofness of leather.

ACKNOWLEDGMENT

The assistance of John Mandel in the statistical analysis of the experimental data is gratefully acknowledged.

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Received October 20, 1959.

Guide to International Information Facilities

The preparation of a guide to international information facilities in science, technology, medicine, and agriculture has been begun by the International Organizations Section of the Library of Congress under a grant from the National Science Foundation. It is estimated that the number of organizations about which information will be sought will be between three and four hundred. The guide will give information on the following topics: name of international organization in English with the language of the enabling act in parentheses, address of secretariat, date of founding and by whom, aims and scope, membership, sources of revenue, and detailed information on communication services (publications, documentation services, and meetings).

The guide is to be published and distributed by the Government Printing Office. The selling price has not yet been determined.

—*Science Information News*, June-July, 1959. National Science Foundation, Washington, D. C.

Abstracts of Chinese Science

Beginning in 1958, the Institute of Scientific Information of the Academia Sinica in Peking initiated the publication *Science Abstracts of China*. This new English language abstract service appears bimonthly in five different series: *Mathematical and Physical Sciences, Chemistry and Chemical Technology, Biological Sciences, Earth Sciences*, and *Technical Sciences*. Each numbered abstract is prefaced by title and author of the paper in English, Chinese title and author in characters, name of journal in Chinese, European language title, year of publication, volume number, and pagination. These abstracts appear to be an excellent source for evaluating the quantity and quality of the contemporary Chinese communist scientific literature. The Institute, at 117 Chao Yang Men Street, Peking, has solicited exchanges for this new publication.

—*Science Information News*, June-July, 1959. National Science Foundation, Washington, D. C.

America's chemical industry had its beginning in Boston in 1635, just 15 years after the Pilgrims landed. As the new nation grew, so did the industry as it developed new products and processes and built new plants. By mid-1959, in terms of assets, it had grown to fourth in size among all U.S. industries.

—*The Chemical Industry Facts Book, 1960-61 Edition*. Manufacturing Chemists' Association, Inc., Washington, D. C.

THE MODE OF COORDINATION OF AMINO ACIDS WITH CATIONIC CHROMIUM IN ACID AQUEOUS SOLUTIONS

II. POTENTIOMETRIC TITRATION

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ABSTRACT

Potentiometric titration curves and precipitation point estimations have been carried out on basic chromium complexes prepared from sodium acetate, glycine, β-alanine, ε-amino-n-caproic acid, and α- β-, and γ-amino-butyric acids. The conclusions drawn are: over the pH range 2.50 to 3.82 and using ratios from 1 to 3 moles acid per chromium, the amine groups are free and not attached to the chromium complex; direct estimations of the approximate amounts of free acids are possible and show no evidence of specific combining proportions over the above range; the general quantitative and stability patterns show a reversible mass action relationship with a trend favouring the amino acids of higher pK_1 values, which is the opposite to that which would be expected if chelation of the amine group was occurring in the α- and β- amino acids. These results confirm the spectrophotometric and miniature tanning studies of Part I of this series (1).

INTRODUCTION

While there now seems to be a considerable mass of evidence (2–7) that the unchelated amine group does not show appreciable coordination to cationic chromium under aqueous acid conditions, two publications of comparatively recent date have suggested that some chelation of the amine group does occur in the case of glycine (7, 8, 9) and alanine (10).

Examination of the data on which these suggestions are based shows that alternative explanations can be offered and that conclusive proof is absent. Thus in comparing acetate ions with glycine, Ramaswamy and Nayudamma (8) have used the method of continuous variation without taking into ac-

count the fact that these ligands have different total charges, which must modify the degrees of olation and hence the spectrophotometric activities of the complexes. Differences in degree of coordination calculated from spectrophotometric data cannot be regarded as proof that the positively charged amine group of glycine has coordinated to an appreciable extent. A more direct attempt at estimating coordination of the amine group of alanine has been made by Green and Ang (9). However they do not appear to have eliminated the possibility that the lower reactivity of the amine group, as shown by van Slyk nitrogen determinations, may have been due to steric hindrance which is likely to be considerable in the α-position to a carboxyl group coordinated to a large olated chromium complex.

In Part I of this series a comparative spectrophotometric study has been carried out of the coordination to chromium of the α, β, γ, and ϵ forms of amino acids, taking advantage of previous work on other bidendate ligands (10–13), which indicates that amino acids such as γ- amino-n-butyric and ϵ-amino-n-caproic would be extremely unlikely to show any chelation involving the oxygen and nitrogen atoms in seven- and nine-membered rings. This spectrophotometric study has indicated that little or no coordination of the amine group appears to take place over the pH range 2.50–3.82 and that stability is related to the pK values of the carboxyl groups of the amino acids.

PRELIMINARY EXPERIMENTAL WORK

Previous work has shown that in the case of the dicarboxylic acids the stability of the rings formed by coordination to trivalent chromium falls sharply from the α to the β forms and that the γ (succinic) and higher forms (e.g., adipic) give precipitates due to the linkage of chromium complexes to produce insoluble chains. Commercial use has been made of the latter observation as a means whereby chromium fixation in leather can be enhanced (e.g., by the marketing of proprietary products such as "Lissatan CH" (I.C.I.) and "Implenal UR" (B.A.S.F.) which are dibasic organic acids.

Preliminary experimental work has failed to reveal any tendency for precipitation over the pH range 2.50 and 3.82 of complexes formed in aqueous solution by the α-, β-, γ- or ϵ-amino acids and 0.3*M* chromic sulphate. Of particular interest were comparisons between the complexes formed by the γ- and ϵ-amino acids and by succinates and adipates where the chain lengths separating the active groups were similar. The freely soluble complexes formed by the γ- and ϵ-amino acids support other evidence that the amine group does not coordinate appreciably to trivalent chromium under aqueous acid conditions.

PREPARATION OF SOLUTIONS

A stock solution of 0.5*M* reagent-grade chrome alum was prepared. Aliquots of this solution were taken, and solutions of the various amino acids

were added in such quantity that the molar ratios of amino acid/chromium were 1, 2, and 3. Three separate aliquots were prepared at each molar ratio for all the amino acids studied (the amino acids used in this work were obtained from L. Light & Co., Colnbrook, U.K.) and were adjusted by the addition of N-hydrochloric acid or N-potassium hydroxide so that the equilibrium pH lay at one of three predetermined values, namely 2.50, 3.16, and 3.82. Equilibrium was attained by alternately adding HCl or NaOH, warming on a hot plate at about 60°C. for 2 hr., cooling, and readjusting the pH until no further adjustment was required after two successive heatings. Each masked chrome liquor so prepared was then made up to volume so that the final solution was 0.33*M* with respect to chromium. It was found that the amount of added water was in the order of only 5% and that it made a negligible alteration to the pH of the solution.

Titrations were carried out with *N* KOH on 4 cc. portions of the chromium solutions diluted to 100 cc. In order to minimise the effects of olation changes and dilution on the pH readings, titrations were performed rapidly and at approximately similar rates for comparative purposes. Titrating alkali was added dropwise from a micro-burette, and stirring was carried out with CO_2-free air. A "Cambridge Bench Type" pH meter was used with the dip-type glass-calomel electrode system; a "Cambridge" wide-range glass electrode (Cat. No. 42558/S) provided accuracy up to pH 12. The use of a micro-burette in conjunction with *N* KOH is the usual technique to avoid the introduction of a volume correction in calculating pH curves, while the quantity of chromium solution chosen was guided by the total alkali needed when titrating 3 moles per Cr of amino acid initially at pH 2.50.

The problem of 25-fold dilution of chromium complexes is encountered in all potentiometric, conductimetric, and spectrophotometric work and advantage is normally taken of the slow rate of change compared with the time taken for titration. This was checked spectrophotometrically in Part I of this series and found to be negligible. The slight change of pH caused by dilution will have an effect on the basicities of the complexes, but as this work is aimed at comparison of complexes under identical conditions using initial pH values 2.50, 3.16, and 3.82, the effects of rapid dilution can be ignored.

RESULTS OF POTENTIOMETRIC TITRATIONS

Figures 1 and 2 show results obtained for 1 mole amino acid/mole Cr aged to equilibirum at pH 3.82 (approximately 50% basicity). The initial parts of the curves have been corrected from blank titration for the small amounts of free acid which titrates initially. For example, free glycine not linked to the complex is half-neutralised at pH 2.3, while free γ-amino-n-butyric acid is half-neutralised at pH 4.2. The amounts of free acid were determined by back titration with HCl and the amounts coordinated are given in Table II.

It will be seen that corrections required in Figs. 1 and 2 were very small, as very little free amino acid was found at 1 mole/Cr and pH 3.82.

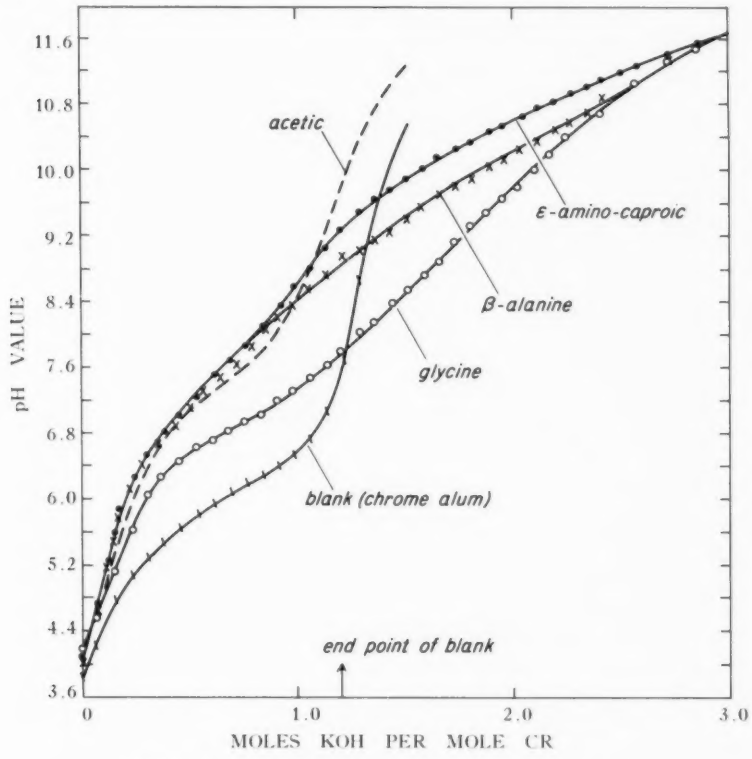

FIGURE 1.—pH titration curves of chromium complexes.

The blank curve on chrome alum shows that the titration of the chromium occurs mainly over the range pH 5.0–7.0 but that the effect of one acetate group per Cr elevates this titration range by producing a complex more stable to alkali. However, the titration curve becomes very steep toward the end of the addition of sufficient alkali to neutralise all available acid groups. Cooper (14) has shown that coordinated amine groups titrated under similar conditions are not displaced by alkali and that the stability of coordination of amine groups to chromium is enhanced by increase of pH. Thus there seems no reason to anticipate that coordinated amine groups should titrate under these conditions. Furthermore the rate of coordination reversal of amine ligands in chromium complexes has been found by him to be very slow.

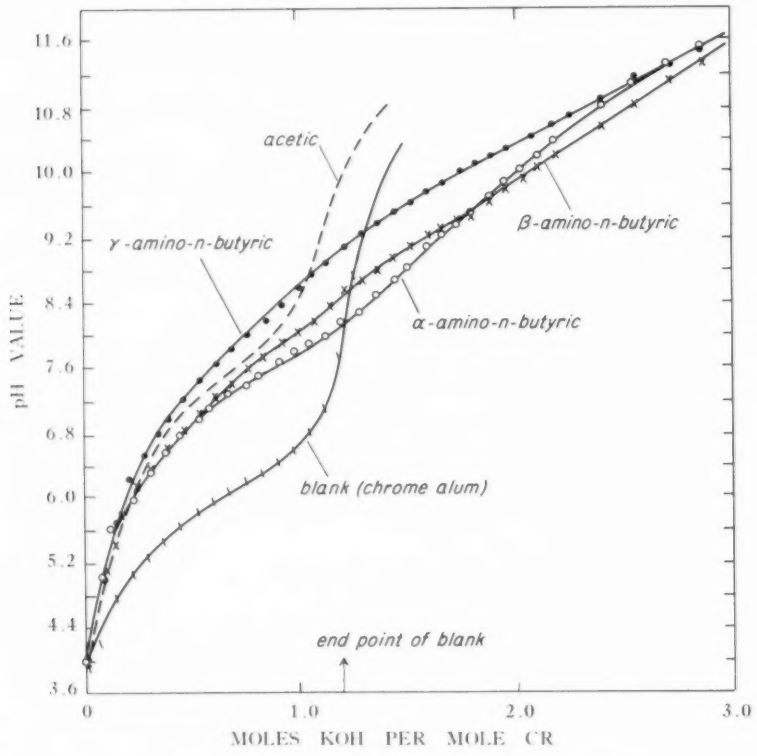

FIGURE 2.—pH titration curves of chromium complexes.

Murphy and Martell (15) have shown that in the case of coordination of glycine to copper, the resulting complex (*see* Fig. 3) behaves like an acid of pK about 4.8, the amount of H ion titrated over this region being equal to 1 equivalent of the ligand. A somewhat parallel occurrence in the case of chromium is the liberation of one equivalent of H ion per mole of lactate in the reaction between sodium lactate and 33% basic chromium sulphate (16), in spite of the aliphatic character of the chelating OH group. The resulting acid has a pK value of the order of 2.0.

Therefore, if a similar chelated complex were formed between an α amino acid and a chromium cation, the anticipated effect should be a transfer of the buffer area from the normal pK_2 region of the amino acid (pH 8.0–12.0) to the acid side (pH 3.5–5.5). Examination of the curves shown in Figs. 1 and 2 reveals no evidence of this. The glycine curve does lie below the

others (although still well above the blank chrome alum curve) but this is accounted for by the low precipitation point (pH 6.0) of the glycine complex. The α-, β-, and γ-amino-butyric acids lie very close together on the acid side, separating in the expected manner on the alkaline side due to the differences in pK_2 values of the free amino acids. The main buffer regions indicate that the bulk of the amine groups are free in all cases.

TABLE I

APPROXIMATE pK VALUES OF AMINO ACIDS (17)

	pK_1	pK_2
Acetic acid	4.6	—
Glycine	2.3	9.6
β-alanine	3.60	10.2
ε-amino-n-caproic	4.4	10.7
α-amino-n-butyric	2.5	9.6
β-amino-n-butyric	3.6	(10.2)*
γ-amino-n-butyric	4.2	10.4

*Estimated value

The extent to which the initial phases of the curves lie above the chrome alum blank can be taken as evidence of increased resistance to alkali titration due to the stabilising influence of coordination, which might be expected to show marked differences between the α-, β-, γ- and ε-amino acids if chelation occurred in the former. The order of increasing resistance to alkali titration was glycine, α-amino-n-butyric, β-amino-n-butyric, acetic, β-alanine, ε-amino-n-caproic, and γ-amino-n-butyric, which is in the approximate order of the pK_1 values, and opposite to the ability to chelate.

The later phases of the curves show that the amine groups are being titrated and follow the approximate order of the pK_2 values but with a general displacement to somewhat lower pH values at the half-neutralisation points. This may be due to the attachment of a portion of the amino acid by carboxyl groups to the chromium, giving rise to lowered pK_2 values as observed in the amino acid esters (16). However, the system is a complicated one, and other factors may be the cause of this effect. The amine groups in all cases are evidently free to titrate, and no trend is apparent in Figs. 1 and 2 which would indicate chelation of the α- and β-amino acids as distinct from the ε- and γ-amino acids.

The titration curves shown in Figs. 1 and 2 were repeated on complexes aged to equilibrium at pH 3.16 and 2.50 and using 2 moles/Cr and 3 moles/Cr of amino acid, making nine curves for each amino acid. The interpretation

became more complicated owing to the presence of free amino acid not attached to chromium, giving interference in the curves which varied according to the pK_1 values. After correction for this, the general findings confirmed the conclusion that if any chelation had occurred in the α- or β- amino acids, this produced no appreciable effects on the stability of the complex towards alkali titration, and the amine groups titrated freely to their calculated end points in all cases.

In order to estimate the amount of free acid, and hence by difference the amount taken up by the chromium, the solutions were back titrated with HCl solution. Owing to the difficulty of determining the total end points at low pH readings, it was found more satisfactory to double the amount of HCl required to reach the pK_1 value of the acid, corrected by a blank titration on the free amino acid. Using this method, back titrations with HCl were only required where the pK_1 values were below the initial solution pH values. The amounts of coordinated amino acid are given in Table II.

TABLE II

MOLES AMINO ACID COORDINATED PER CR

Moles Added	1/Cr			2/Cr			3/Cr		
pH of Aged Soln.	2.50	3.16	3.82	2.50	3.16	3.82	2.50	3.16	3.82
Glycine	0.5	0.6	0.8	0.7	0.7	0.9	0.7	0.9	1.1
β-alanine	–	0.7	0.9	0.7	0.7	0.9	0.8	1.1	1.2
ϵ-amino-n-caproic	0.6	0.8	0.9	0.8	0.9	1.1	0.9	1.3	1.5
α-amino-n-butyric	0.5	0.7	0.9	0.7	0.9	1.0	1.0	1.2	1.3
β-amino-n-butyric	–	0.7	0.9	0.8	0.9	1.0	1.0	1.1	1.5
γ-amino-n-butyric	0.6	0.8	0.9	0.8	1.0	1.1	1.0	1.4	1.6

It is apparent from this table that the amounts of amino acids coordinated to chromium over the pH range 2.50 to 3.82 were not enhanced by the α or β positions of the NH_2 groups as compared with the ϵ or γ positions. The trend appears to follow the approximate pattern of the pK_1 values of the carboxyl groups of the amino acids (*see* Table I). It should be noted that, although these estimations of coordinated acid by back titration of the free acid to the pK_1 values are approximations, they are replicated 52 times in Table II, so that the general pattern is correspondingly more reliable.

A further indication of the relative stabilities of the complexes is given by the pH values at which the first signs of precipitation were observed during the alkali titration curves. These are given in Table III.

The poor stabilities to alkali of the glycine complexes is particularly striking. Again there is no indication that the α or β positions of the amino

TABLE III

pH VALUES OF INITIAL PRECIPITATION POINTS

Moles Added	1/Cr			2/Cr			3/Cr		
pH of Aged Soln.	2.50	3.16	3.82	2.50	3.16	3.82	2.50	3.16	3.82
Na Acetate	6.2	6.2	6.3	6.3	7.4	>10	6.5	>10	>10
Glycine	6.0	5.8	6.0	6.2	6.5	6.6	6.6	7.2	9.0
β-alanine	6.5	7.0	7.9	6.5	8.6	9.6	8.1	9.0	9.2
ε-amino-n-caproic	6.5	8.6	>10	6.5	10.0	>10	>10	>10	>10
α-amino-n-butyric	6.5	8.1	9.5	6.5	9.5	>10	>10	9.5	>10
β-amino-n-butyric	6.5	9.1	>10	7.0	9.5	>10	>10	>10	>10
γ-amino-n-butyric	6.5	8.4	9.5	6.5	9.5	>10	>10	>10	>10

group confer added stability; in fact, the trend is in the reverse direction, the acids with higher pK_1 values providing the more stable complexes, in spite of their comparatively reduced degrees of ionisation at the pH values at which the chromium complexes were formed.

DISCUSSION

It is evident from the above results that approximate estimations can be made of the amounts of amino acids coordinated, by the direct method of potentiometric titration of the residual free acid. Although only approximate, this may well be sounder than applying the method of continuous variation spectrophotometry to chromium complexes where small changes in olation or pH can give rise to large alterations in optical characteristics.

It is also noteworthy that the data show no indication of definite combining proportions of amino acid and chromium complex, as suggested by Green and Ang (9). The pattern is typical of a reversible mass action relationship, although it is possible that more decisive combining proportions might occur at higher pH values.

In considering the probability of chelation of the amine group, it should be noted that ring formation between the two oxygen atoms of the carboxyl group and the olated chromium complex provides the competitive alternative, as shown in Fig. 3. In this respect chromium differs from metals which do not form stable olated compounds.

Although only one negative charge is distributed between two oxygens in the carboxyl group chelated ring, this may well be more stable than a ring formed under acidic conditions where the amine group and the chromium complex are both positively charged. An appreciable change in the charge of the amine group is unlikely below pH 7.0 as the pK_2 values range from

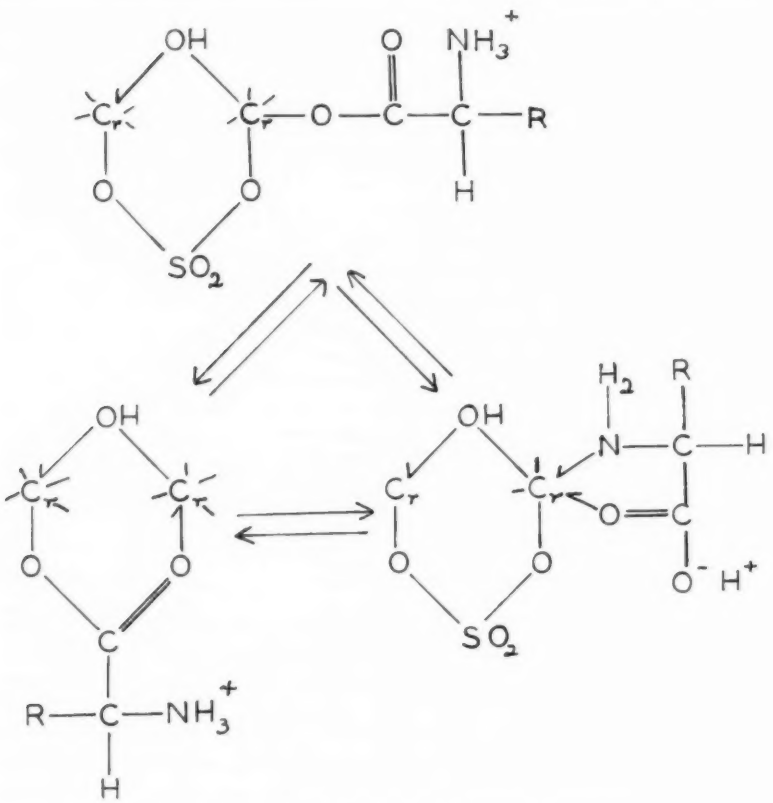

FIGURE 3.—Possible α-amino acid chromium complexes.

9.6 to 10.7. In the case of the dicarboxylic acids, chelation of the α and β forms occurs because two negatively charged oxygens are available in suitable spatial orientation.

CONCLUSIONS

The following conclusions are drawn:

1. The absence of precipitation under acidic conditions of the basic complexes formed by trivalent chromium with the γ- and ε-amino acids indicates an absence of chain formation between complexes, while the improbability of formation of seven- and nine-memberd rings suggests that

no amine group combination or chelation takes place with these amino acids over the pH range 2.50 to 3.82.

2. This is confirmed by the potentiometric titration curves where the amine groups are shown to titrate freely.

3. The complexes formed by the α- and β-amino acids showed no evidence of increased resistance to reaction with alkali as compared with the γ- and ε-amino acids, and the amine groups were equally free to titrate.

4. The amounts of amino acids coordinated to chromium between pH 2.50 and 3.82 showed no trend in favour of the α or β positions as compared with the ε or γ positions.

5. The precipitation points during alkali titration showed no trend indicative of chelated amine groups as the glycine complexes precipitated at lower pH values than the corresponding acetate complexes.

6. There was no indication of favoured combining porportions between amino acid and chromium ions over the pH range 2.50 to 3.82 and the ratios from 1 to 3 moles amino acid per chromium. The general quantitative and stability patterns were typical of a reversible mass action relationship with a trend favouring the amino acids of higher pK_1 values.

7. These results confirm the spectrophotometric titration and miniature tannage studies of Part I of this series of papers (1).

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Received July 8, 1959.

LIFE LINES

Brief Biographies of Our Contributors

THOMAS J. CARTER received the B. S. degree from Benedict College, Columbia, South Carolina, and has continued his education at Howard University and American University in Washington, D. C. He came to the National Bureau of Standards in 1943 and since that time has been active in the development of test methods and apparatus for the evaluation of leather and leather products. He became a member of ALCA in 1952.

CONRAD L. ORNES received his chemical engineering degree from the University of Cincinnati in 1924. Except for a five-year period spent in teaching as head of the chemistry department of the Ohio Mechanics Institute in Cincinnati, he has acquired all of his chemical experience in the leather industry. He was chief chemist at the American Oak Leather Company for many years, followed by a brief period with the A. C. Lawrence Leather Company. He is now a research associate at the Tanners' Council Laboratory at the University of Cincinnati.

WILLIAM T. RODDY, a graduate of the University of Cincinnati, has been associated with the Tanners' Council Research Laboratory for over 25 years. Since joining ALCA in 1939 he has been an active member, serving on the Physical Testing Committee, the Preparatory and Posttanning Processes Committee, and the Council. His numerous contributions to *JALCA* as well as other journals have added much to our knowledge of the structure of skin, beamhouse processes, tanning, and posttanning operations. Professor Roddy received the coveted Alsop Award at the 1957 ALCA Annual Meeting.

DR. S. G. SHUTTLEWORTH graduated from Rhodes University in 1930. He obtained his Master's and Doctor's degrees from the same University in 1935 and 1937. He was the first Proctor Memorial Fellow at the University of Leeds in 1939 and later held the Hunt Rankin Fellowship at Lehigh. After a short period as Technical Director of Bona Allen Co., Georgia, he returned to South Africa in 1941 to assume directorship of the newly established Leather Industries Research Institute, a position which he still holds. Dr. Shuttleworth's principal interest has been in the field of chrome chemistry, and he has published over 200 scientific papers and reports on various aspects of the hide and skin, leather and footwear industries. He is a Fellow of the Royal Institute of Chemistry and of the British and South African Boot & Shoe Institutes.

DR. R. L. SYKES graduated with First Class Honors from Leeds University in 1950 and received his Ph.D. from the same institution in 1952. He was awarded the LeBlanc Medal by the Faculty of Technology of Leeds (1950), held the Proctor Memorial Fellowship (1950-51), and received the Donald Burton Prize of the Society of Leather Trades' Chemists in 1953. After 18 months in the British Colonial Service in East Africa, where he worked in an advisory capacity to the hides, skins and leather industries, he joined the Leather Industries Research Institute, Grahamstown, South Africa, as Senior Research Officer in 1954. His brief professional career has already resulted in a score of publications in various technical and scientific journals.

The National Bureau of Standards 1957 annual report declares that results of recent work showed that the amount of chrome combined at 50°C. was 3 to 4 times greater than that combined at 0° C. An analysis of the data indicated that the sulfate (SO_4^-) combined in the leather consisted of two components: one which was constant at all temperatures, and one which varied in the same ratio with the amount of chrome (Cr_2O_3) at all temperatures. The first component had combined with free basic groups in the leather protein, and the second was combined in the chrome tanning complex. The formation of the chrome tanning complex depends on hydrolysis which increases with increase in temperature. The influence of temperature, therefore, may be explained from the increase in the rate of hydrolysis, which produces more active chrome complexes to combine with the collagen.

Organic and fibrous materials, when placed in water, evolve heat. The source of the heat is assumed to be the reaction of the water with certain active groups present in the materials. Measurement of this heat of wetting in a calorimeter provides a quick, simple procedure for obtaining an over-all estimate of the water adsorptive properties. High water adsorptive capacity contributes to the comfort-giving qualities of natural and synthetic fibers used in the manufacture of footwear and clothing.

The application of scientific principles to the tanning of hides was not generally accepted until about the beginning of the twentieth century. Most of the early research on leather by industrial and Government scientists was devoted to measuring physical properties, standardizing test procedures, and improving the serviceability of leather, particularly for footwear.

A broad program of leather research and development, of interest to Government agencies and private industry, was initiated at the National Bureau of Standards prior to World War I. The increased volume and importance of this work was recognized March 1, 1926, by the formation of the National Bureau of Standards Leather Section.

—*Leather Research and Technology at the National Bureau of Standards*, U. S. Department of Commerce, NBS circular 560.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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PAPERS FOR ANNUAL MEETING

Members and others wishing to present papers at the ALCA Meeting, June 19–22, 1960, should submit abstracts for consideration by the Convention Committee. These should be sent to Dr. Robert Stubbings, Division of Leather Technology, Lehigh University, Bethlehem, Pa., to arrive not later than April 1.

FIFTY YEARS OF SERVICE TO THE LEATHER INDUSTRY

A lifetime of service to the leather industry came to a close on January 2, when Otto Haas, president of Rohm & Haas Company, Philadelphia, for fifty years, died at his home in Villanova, Pennsylvania.

Mr. Haas was born in Stuttgart, Germany, on March 15, 1872. He came to the United States in 1902 and was associated with a meat packing firm which dealt in the export of meat and hides. This was the beginning of an interest in the leather industry which was continued throughout his life.

In 1905 Mr. Haas received a letter from Germany which ultimately led him into the manufacture of leather chemicals. Dr. Otto Rohm, a friend and subsequent business associate, wrote that he had developed Oropon—the first prepared enzymatic bate for leather processing. He suggested that Mr. Haas join him in the formation of a partnership for the development of this product. Otto Haas accepted the proposal with the reservation that he would remain in Europe only so long as it was necessary to establish the new enterprise there. He went back to Germany, and in 1907 the Rohm & Haas partnership was established. Two years later—the partnership having proved successful—Mr. Haas returned to the United States and founded the American firm. Dr. Rohm remained in Germany as head of the German company.

Under the energetic leadership of Mr. Haas the business prospered in America, and in time the company was incorporated as an American firm. Mr. Haas was keenly aware of the need for technical service to aid the leather industry in making use of the new techniques in tanning which Oropon made possible, and he was no less cognizant of the contributions which chemical research should be able to make to leather manufacturers. Laboratory facilities were established, and soon, through this pioneering research effort, other products for leather processing were developed, including such products as dimethylamine sulfate for unhairing of hides, synthetic tanning agents which assist or replace natural vegetable tans, zirconium salts for tanning white leather, and a wide range of finishing materials. Products for other industries include acrylic plastic sheet and molding powder; resins for coatings and other applications; chemicals for textile processing; agricultural chemicals; and a wide range of other chemical materials.

The expansion of the company's activities into new fields did not lessen the interest which Mr. Haas maintained in the leather industry. He counted among his personal friends a host of leathermakers across the country.

Mr. Haas remained active head of the company he founded for a full fifty years. Only three days before his death he had asked to be relieved of his duties, due to failing health. Complying with this request, the Board of

Directors, in a special meeting on December 31, 1959, elected Dr. F. O. Haas, son of the founder, President of the company; Dr. Ralph Connor, Chairman of the Board; and Mr. John C. Haas, also a son of the founder, Vice Chairman of the Board.

In addition to the two sons listed above, Mr. Haas is survived by his wife, Phoebe W. Haas, and seven grandchildren.

COUNCIL MEETING MINUTES

January 15, 1960
Plankinton House

Milwaukee, Wisconsin

The meeting was called to order by President Maeser with the following officers present: Messrs. Henrich, Retzsch, Somerville, Edmonds, Presley, Tetreault, and O'Flaherty. Also the following guests were present: Messrs. Compton, Klimpl, Martin, Meo, Stubbings, Turley, T. Thorstensen, Wederbrand, and Windus.

The minutes of the Council Meeting held on October 8, 1959, were read and approved.

The report of the Technical Committees was read by Dr. R. Henrich. Upon motion made, duly seconded, and unanimously approved, it was ordered that the report be published.

A report by the Editor, Dr. W. Windus, was read and unanimously approved.

After some discussion it was decided that effort will be made to obtain such technical papers as are given at the various Production Clubs for original publication when appropriate in the *Journal*.

Dr. R. Stubbings presented a report on the 1960 Annual Meeting. Council discussed the chairmanship of the symposium and rules concerning golf prizes. The report was unanimously approved upon a motion by Mr. Retzsch seconded by Mr. Edmonds. The matter of a chairman for the symposium was reported by President Maeser. Mr. G. Walter Schultz has accepted the chairmanship, and he will be assisted by Messrs. Kay and Wagoner.

After hearing that all hotels now scheduled have projection lanterns which are either furnished free or on a rental basis, Council agreed to rescind the order to purchase such equipment for the Association.

President Maeser reported that he had obtained a speaker for the banquet.

It was agreed that the John Arthur Wilson Memorial Lecture be given after the President's report at the first day's morning session. Dr. John H. Highberger has accepted the honor of giving this lecture in 1960.

Mr. Wederbrand reported that seven firms have already subscribed to booths and that he has three more booths which he hopes to find sponsors for.

Mr. Wederbrand, Chairman of the Ways and Means Committee, presented a proposed budget for the Association's 1960 operations. After three minor changes it was approved as published herewith.

In a report on the advertising, it was stated that three advertisers had discontinued their insertions in 1960 and six new advertisers had entered into contracts.

The matter of the Directory costing more than the revenue received from the advertisers was discussed, and Council approved a charge of $15.00 for a quarter-page insertion in the 1960 issue.

The Nominating Committee Chairman, Dr. Ell Dee Compton, reported the following slate of candidates:

FOR PRESIDENT-ELECT

F. Leslie Collins
Robert Stubbings

FOR COUNCIL

Charles F. Dudley
R. M. Lollar
C. W. Mann
T. C. Thorstensen

Council approved the nominations. This slate of candidates will be published in the *Journal* along with Section V(c)* of the By-Laws which informs members how they may present additional candidates.

Dr. Thomas Thorstensen, Chairman of the Awards Committee, made a report for his committee which was approved by Council.

Mr. Edmonds presented a brief report on the several hotels available for the 1964 Annual Meeting. Council requested him to get further details on

*ARTICLE V. SECTION (2)c — Additional candidates may be nominated by petitions signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

the hotel at Quebec and to report at the next meeting. The Secretary was instructed to send a post card to all members, with the next mailing, to determine how many would be able to attend if a meeting were held in Quebec.

A very lengthy discussion on the biennial meeting of the International Union of Leather Chemists followed. The advice of Harold Turley, Charles Martin, and Dominic Meo was very helpful. Council then adjourned for lunch, thus allowing time for each member of Council to give serious thought to the matter. After lunch the discussion was continued and all aspects were considered, i.e., dates, place, etc. Upon a motion made by Mr. Tetreault, seconded by Mr. Retzsch, and unanimously passed, it was decided that President Maeser will extend an official invitation to the President of the International Union of Leather Chemists to hold the 1961 meeting in the United States. It was decided that the meeting should be held in conjunction with our regular Annual Meeting in one of the following cities: Boston, Philadelphia, or Washington, D. C. Mr. Meo was asked to inquire in Washington, D.C. and Boston, and Mr. Wederbrand is to inquire in Philadelphia, to determine whether hotel accommodations can be had at a good hotel some time in the latter part of June. This information is to be obtained as soon as possible, and Council will hold a meeting to make the final decisions. Mr. Meo has agreed to accept the chairmanship of this meeting.

The Secretary read the list of members who were dropped for nonpayment of dues, members who have resigned, and members who have passed away.

There being no further business to be considered, the meeting adjourned.

Respectfully submitted,

FRED O'FLAHERTY

Secretary

ADDITIONAL CANDIDATE FOR THE 1960 ELECTION

Upon petition by members, in accordance with Article V, Section (2)c of the By-Laws, the following nominee for Member of Council has been added to the slate of candidates on the 1960 ballot:

Harold Y. Miller

BUDGET FOR 1960

GENERAL ACCOUNT: INCOME	1959 Proposed	1959 Actual	1960 Proposed
Dues	$11,400.00	$11,174.00	$11,200.00
Interest on United States Bonds	1,275.00	1,300.00*	1,350.00
Methods	50.00	93.40	75.00
Annual Meeting	–0–	–0–	–0–
Directory	750.00	850.12	1,225.00
Total	$13,475.00	$13,417.52	$13,850.00
GENERAL ACCOUNT: EXPENSE			
Executive Secretary's Office	$ 4,600.00	$ 4,600.00	$ 4,600.00
Secretary's Office Expense	1,200.00	739.73	1,000.00
Annual Meeting	500.00	176.64	500.00
Committee Work	100.00	10.00	100.00
Council Meeting	125.00	77.00	125.00
Audit	200.00	200.00	200.00
Printing of By-Laws and Methods	200.00	674.20	200.00
Printing of Directory	975.00	1,064.49	1,100.00
Reserve for Uncollectible Accounts	500.00	375.00	400.00
Winheim Award	100.00	–0–	100.00
Total	$ 8,500.00	$ 7,917.06	$ 8,325.00
Surplus on General Accounts	**$ 4,975.00**	**$ 5,500.46**	**$ 5,525.00**
JOURNAL ACCOUNT: INCOME			
Advertising	$13,650.00	$14,057.92	$14,300.00
Subscriptions	6,150.00	6,026.31	6,000.00
Journals, Volumes, Reprints	2,000.00	3,012.90	2,500.00
Dues, S.L.T.C., Difference	800.00	747.50	750.00
Total	$22,600.00	$23,844.63	$23,550.00
JOURNAL ACCOUNT: EXPENSE			
Printing and Publishing	$19,500.00	$21,038.28	$21,500.00
Printing Reprints	2,000.00	2,237.10	2,200.00
Copyright, Insurance, Storage	500.00	458.00	500.00
Abstracts and Translations	450.00	390.04	450.00
Editor-in-Chief Compensation	600.00	600.00	600.00
Editor-in-Chief Office Expense	400.00	146.56	400.00
Managing Editor Compensation	2,500.00	2,499.96	2,500.00
Managing Editor Office Expense	400.00	359.84	400.00
Advertising Discount Allowed	150.00	147.65	150.00
Total	$26,500.00	$27,877.43	$28,700.00
Deficit on *Journal* Account	**$ 3,900.00**	**$ 4,032.80**	**$ 5,150.00**
Difference (Surplus)	$ 1,075.00	$ 1,467.66	$ 375.00
Reserve for delegate to attend International Meeting	$ 1,000.00	$ 1,000.00	

*Interest from 5 series "F" bonds still to be added to this figure.

CONVENTION COMMITTEE REPORT

The members of the 1960 Convention Committee are:

Robert Stubbings—*Chairman*
Fred Klimpl—*Vice Chairman*
Harold Miller—*Entertainment*
Ben Grota—*Publicity*
Barry Hartnett—*Golf*
Mrs. Helen Thorstensen—*Ladies' Committee*

The following agenda is proposed:

Sunday, June 19
Council Meeting
Committee Meetings
President's Reception

Monday, June 20
A.M.—Technical Papers
P.M.—Golf Tournament
Evening—Dance and Entertainment

Tuesday, June 21
A.M.—Technical Papers
P.M.—Technical Papers
Evening—Banquet

Wednesday, June 22
A.M.—Symposium on Vegetable Tanning
G. W. Schultz, *Chairman*

The proposed budget is:

Registration (350 members @ $8.00)		$2,800.00
(50 nonmembers @ $15.00)		750.00
Exhibit Booths @ $100.00		900.00
		$4,450.00
Registration Expenses	$ 350.00	
Transcription Expenses	600.00	
Speaker	500.00	
President's Reception	1,200.00	
Entertainment	500.00	
Ladies' Committee	300.00	
Golf Committee	300.00	
Miscellaneous	300.00	
	$4,050.00	
Surplus	$ 400.00	

ROBERT STUBBINGS
Chairman, 1960 Convention Committee

ALCA-ASTM JOINT COMMITTEE ON LEATHER

Meeting November 12–13, 1959

Benjamin Franklin Hotel
Philadelphia, Pa.

The subcommittee and section meetings began at 10:00 A.M., November 12, and continued to 2:00 P.M., November 13.

The Advisory Committee met at 4:00 P.M., November 12, to discuss the matters described in the following report.

The Joint Committee convened at 2:00 P.M., November 13. Reports were presented of meetings of subcommittees and sections as well as of the Advisory Committee. Copies are appended. In addition to the change in schedule of subcommittee meetings mentioned in the Advisory Committee report, plans were made to include the proposed half-day discussion of a subject of general interest at the next meeting of the Committee, which will be held in Philadelphia at the Benjamin Franklin Hotel, March 17–18, 1960.

C. W. MANN
Secretary

ADVISORY COMMITTEE

A meeting of the Advisory Committee was held at 4:00 P.M., November 12, 1959. The following members were present: F. Y. Speight, M. Maeser, E. D. Compton, R. L. Young, R. Stubbings, M. H. Battles, M. M. Baldwin, C. W. Mann, B. L. Lewis, and J. R. Kanagy

A committee was selected to review the by-laws. Members are: B. L. Lewis, Chairman, M. Maeser, and E. D. Compton.

A nominating committee for the selection of a new slate of officers to take over in June was selected. This consists of M. M. Baldwin, Chairman, R. M. Lollar, T. C. Thorstensen, G. A. Butz, and C. W. Mann.

There was a discussion of the slow progress in the approval of test methods for promulgation by the ASTM. The exact duplication of ALCA methods for promulgation as ASTM methods was considered unjustified, since further use and publicity for some of them was believed unwise. At the suggestion of F. Y. Speight, it was decided to expand the annual report for 1959 to include a reference to all ALCA methods which the various sections are now considering or on which studies are being made. This will then provide the ASTM with a document containing references to a well-rounded series of methods for determining the physical properties of leather.

The matter of conflicts in the scheduled meeting times of the various sections was discussed. It was decided that henceforth the six most active sections, which consist of Tensile, Properties, Water Resistance, Miscellaneous Properties, Surface Characteristics, and Research and Deterioration, would have at least two hours for meeting time without conflict with any of the other five. The section chairmen were urged to abide by a fixed agenda and complete their most important business within this allotted time. Rooms will be provided at all meetings for informal gatherings of section members.

The meeting was adjourned at 5:30 P.M.

J. R. KANAGY

SUBCOMMITTEE AND SECTION REPORTS

Subcommittee I. Nomenclature, Definitions and Applicability.—Since there were no methods for Subcommittee I to consider, we had no report to submit to the main committee on November 13. However, informally we did agree that the methods to be considered by us should either contain literature references which would justify the significance and precision sections or be accompanied by data to justify these sections.

It was also suggested that unpublished data which justify a method should be filed with the American Documentation Institute so that the data will be available to all.

ROBERT M. LOLLAR

Subcommittee II. Sampling and Conditioning for Physical Testing.—The subcommittee met to discuss two proposed methods for sampling leather for physical tests and the question of preparing a procedure for guidance in research and development.

The second draft of the method of sampling cattlehide leather (except sole leather) for physical tests was discussed. The draft was approved with a few minor changes and will be forwarded for review by Subcommittee I.

The first draft of the method of sampling leather from small skins for physical tests was discussed. A few changes were suggested that will be included in the second draft for review before the next meeting.

Sampling for research and development tests was discussed, but the subcommittee was uncertain on the proposal to prepare this type of method. It was agreed that a draft would be prepared for review and furuther consideration.

C. W. MANN

Subcommittee III.—*Section 2. Physical Dimensions.*—This section had no new business to discuss and did not hold a formal meeting. However, the work of the section is, for the most part, completed. It was assigned to prepare methods on four phases of physical dimensions: (1) Test for Area of Leather, (2) Test for Width of Leather, (3) Test for Thickness of Leather Test Specimens, and (4) Test for Thickness of Leather Units. Proposed methods have been prepared on all of these. Methods 1 and 2 were made tentative in 1957. Methods 3 and 4 were submitted to a letter ballot of the membership of the Joint Committee in October, 1959, and approved with only two negative votes. The negative votes, both objecting to proposed dimensions of the apparatus, are being resolved.

J. Naghski

Section 3. Tensile Properties.—The business of the meeting consisted of the following:

1. It was approved that the Tongue Tear Resistance Method be tabled and the Slit Tear Resistance Test be written up to replace this method; that the Buckle Tear Strength Test be combined with the Stitch Tear, Single Hole Method; and that the Elongation Method for Measuring by Bench Marks on the Samples be tabled and the methods for the elongation measurement between jaws be adopted.

2. Method on Slit Tear Resistance: It was moved that the slit tear specimen be dropped and the slot tear specimen be adopted. Suggestions and changes were made on the method that was passed out to the members present, and it was found that the method was satisfactory for the portion that has been written. Preliminary tests will be made on samples cut from one die. Dies are being made for various members of the Joint Committee; then different types of leather samples will be sent to them for cutting. A round-robin test will be made to establish the decision of accuracy of this method.

3. Method on Stitch Tear Resistance, Single Hole (Buckle Tear): Suggested changes were made and will be rewritten into the method for future adoption. Data will be sent to Mr. Mandel to evaluate for the Precision and Accuracy Section of this method.

4. Methods on Bursting Strength, Ball, and Mullen Grain Crack Tests were discussed at the meeting. The necessary changes that were suggested will be made, and the methods will be ready for adoption as soon as the precision and accuracy can be established.

5. The Stitch Tear (Double Hole) and Tensile Strength methods are in process and will be ready for the Precision and Accuracy sections as soon as the data are sent in for processing.

6. There were suggestions by the members attending this meeting that the thickness should be specified in thousandths of an inch instead of the other measurements that are shown, such as ounces, irons, etc.

7. In the Tensile Strength Method it was decided that we should leave the die at the present dimension instead of three sizes as stated previously. Changes will be made at a later date when the data Mr. Maeser has are received and evaluated.

8. Also there would be some tests made to see if there is any difference in the measurement of elongation by the Bench Mark Method or by the Jaw Separation Method.

9. The progress of the work in this committee indicates that we will have methods ready for approval by the Joint Committee at the next meeting.

R. L. YOUNG, JR.

Section 4. Measurement of Water Resistance.—The Method for Water Absorption, Static, has been approved by Committee I and submitted to the Editorial Committee.

The Spray Test for Garment Leather is now being considered by Committee I.

A method for the Water Absorption of Garment Leather using whole skins will be submitted to Committee I for approval.

The Dynamic Method for Heavy Leather is now in the hands of Arthur Kay and will be passed on to J. Wagoner as soon as tests are completed.

Adjacent samples from each of two sides of four types of upper leather and three types of sole leather have been tested in the laboratories of the Bureau of Standards and Endicott-Johnson in the Kubelka apparatus. Dr. Kanagy will furnish a statistical analysis of these results to determine whether or not further consideration is warranted.

Considerable discussion was held regarding the two alternate methods for Dynamic Water Penetration, Absorption, and Transmission as applied to upper leather. Charles Dudley will endeavor to incorporate these further suggestions into the two methods which will again be sent to our committee for approval.

Further interest was expressed in the rate of drying of different types of leather having the same moisture content. Dr. Kremen has some work in progress in this field, and we will await a further report from him.

Charles Dudley outlined the program which he has under way toward a method for determining the water resistance of finished shoes. The committee recommended one change in the procedure as outlined.

Definitions of *water resistance*, *water-repellent*, and *waterproof* will be circulated to our committee for approval so that they may be added to the dictionary of terms which is being prepared.

R. G. Ashcraft

Section 5. Leather Lightfastness Test.—Round-robin tests of fading in various Fadeometers, under Hanovia lamps, and in outdoor exposure in South Florida were completed, and partial results were studied by the subcommittee. A complete report will be sent to all members of Section 5 in the near future so that action can be taken by the March meeting on a new series of tests.

Flex Testing of Finish on Upholstery Leather.—Data on precision and reproducibility are being collected. The method has been approved by the subcommittee and will be submitted to the Applicability Committee as soon as these data are assembled.

Cold Crack Resistance of Upholstery Leather.—The method has been approved by the subcommittee and by the Applicability Committee and now is being revised after being sent back by the Editorial Committee.

Crock Test.—A round-robin test of various laboratories using various modifications of the AATCC crockmeter has been started.

Scuff Test.—A preliminary test of various scuff-testing devices has been started.

Bleeding Test.—Data about various available methods are being collected for future subcommittee work.

No other test methods are under active consideration by the subcommittee at present, although preliminary studies are being made concerning the applicability of the Flex Test for Finish on leathers other than upholstery.

R. Stubbings

Section 6. Fire Resistance.—Inactive.

Section 7. Mechanical Leathers.—A meeting of the section was held at 1:00 P.M. on November 12, 1959. Present were two regular members and two guests.

The proposed Method to Determine the Area Stability of Leather in Water and Oil, as drawn up under the date of October 1, 1959, was discussed, and a few changes were made. The procedures are applicable to insole and mechanical leathers.

Regarding precision, it has been suggested that 20 test pieces each be sent out by the writer to two or three laboratories in order to determine the standard deviation on the basis of 20 tests. These test pieces will be sent out shortly.

The changed version of the proposed method has been sent to Dr. Lollar for his review and comments.

A. HIRSCH

Section 8. Deterioration Effects.—The following subjects were discussed:

1. *Heat Stability Under Conditions of Pressure and Heat.*—This was the first consideration of this area by the committee. A group of three (C. Mann, G. Ashcraft, and C. Dudley) will study the area and report recommended action to the committee.

2. *Heat Stability Project.*—J. Cassell discussed the status of this project. The Bureau of Standards has been investigating rapid moist-tropical aging. Dow Corning will study dry-desert conditions. The results of the rapid tests will be compared to data on the same leathers exposed in the QM Climatic Chambers.

Straight vegetable-tanned leather will be added to the straight chrome and chrome-vegetable retan leathers already under consideration. The eight leathers are now in the Climatic Chambers. Tests will be made at 0, 4, 12, and 24 months.

Moist-tropical conditions to be used will be 60°C. at 95–100% RH. Dry-desert conditions will be studied at 100°C. at 10–12% RH and 100°C. at 1–5% RH.

Both stitch tear and bursting strength will be used to evaluate deterioration.

3. *Upper Leather Perspiration Project.*—W. Roddy reviewed the report submitted to the group on June 25, 1959. The leather used in this initial test to evaluate the Roddy-Lollar Method showed little deterioration.

Commercial leathers that exhibit poor resistance to this test will be obtained, and the latter laboratory testing will be repeated.

Both the Mullen Test for Grain Crack and a qualitative evaluation of shrinkage, color change, and temper will be used.

Two shoe manufacturers have indicated to the committee that the Roddy-Lollar Method is used by their organization to obtain acceptable white leather.

CHARLES F. DUDLEY

Section 9.—Disbanded.

Section 10. Miscellaneous Physical Properties.—The development of a shrinkage temperature method that would measure shrinkage temperature of leather above 100° C. was discussed, and three devices were proposed to facilitate measurement. These included:

a. The Maeser Closed Capsule
b. The Kremen Container
c. The Mann Transverse Shrink Meter

Maeser and Kremen will provide drawings or photographs of their devices; and Mann will write up his method and indicate the cost of the instrument and a commercial source.

Definitions of break and pipeyness were presented, and there did not appear to be very much difference in the language describing the characteristics.

The temper characteristic of leather was discussed, and an attempt was made to arrive at a definition or understanding of the property. The definition and the need for a method of evaluating temper were not resolved. In the case of unlined shoes, it was agreed that a stiffness quality was important to maintain the appearance of this kind of footwear.

A method for simultaneously evaluating the wear and water resistance of sole leather by means of the Universal Leather Tester, an instrument developed by the U.S. Naval Research and Development Facility, Brooklyn 32, N.Y., was disclosed. The instrument arrives at end points electronically; and mils wear per thousand cycles are determined as well as the number of cycles required to affect water penetration through the sample.

Methods previously approved by the subcommittee will be written up and submitted to Dr. Lollar's section, pending evaluation of precision.

MILTON BAILEY

Subcommittee IV. Research.—The following members were present:

R. G. Ashcraft
Milton Bailey
M. H. Battles
N. C. Benrud
E. D. Compton
A. W. Hopton
J. R. Kanagy
S. S. Kremen
R. M. Lollar
Mieth Maeser
C. W. Mann
W. T. Roddy (representing Fred O'Flaherty)
L. P. Witnauer
M. M. Baldwin (Chairman)

Visitors included:

R. J. Carrol
J. M. Cassel
C. F. Dudley
E. Filachione
H. Hodus
B. L. Lewis
M. H. Olson
R. Stubbings
S. T. Tu

The first item on the agenda was consideration of a program of papers for the 1960 spring meeting of the entire committee. The chairman reported that an insufficient number of suggestions was received in time to schedule a program at this November meeting. Suggestions received were: a preview of Snyder's paper on "Thermal Conductivity of Various Shoe Materials", a discussion of the Kubelka method for water absorption, a report on some performance criteria in the evaluation of sole leather and on visual criteria in the evaluation of upper leather, a report on DMS leather boots, and a report on the objectives and projects of Section 8 (Deterioration). It was brought to the attention of the subcommittee that the Advisory Committee had suggested that the program for the next several meetings include a review of the work and objectives of the various sections. It was the consensus of the subcommittee that the chairman should arrange for a program along this line.

A method for measuring the electrical conductivity of leather was described by Mr. Kremen. He pointed out the significance of such a test for sole leather to be used in certain types of safety shoes. Discussion brought out subcommittee consensus that this is an important property of leather and that we should recommend to the Advisory Committee that a suitable method should be formulated for eventual adoption by the Joint Committee. It was pointed out that such a method may be very similar to an ASTM method for plastics.

Dr. Kanagy discussed data obtained on heat of wetting of leather and other materials and pointed out the correlation of these heat values with the

corresponding water sorption capacities. Relative to the relationship between heat of wetting and comfort factors it was suggested in discussion that the amount of heat involved in normal leather moisture variation probably would not be enough to have an appreciable influence on the comfort factor.

Moisture absorption in the foot-sock-shoe system was reviewed by Mr. Mann. He cited in particular the article by Gunnar Gran on "Investigations on Shoe Climate and Foot Comfort" (*J. Soc Leather Trades' Chemists*, **43,** 182–96 [1959]). It was suggested that rate may be important in the transfer of moisture from one part of this system to another. It was recommended that this subject should receive further consideration. Dr. Stubbings, Mr. Battles, and Dr. Witnauer will look into the subject of water sorption in relation to comfort and report at the next meeting of the subcommittee. The somewhat tangential question was raised as to whether the committee should concern itself with methods for testing end use items.

Dr. Kanagy reported that work on comparison of the Bureau of Standards Method with the Cenco Fitch Method for Measurement of Heat Conductivity is in progress and results will be reported at the next meeting of the subcommittee.

There is continued interest in the application of nondestructive test methods to leather, particularly in sonic methods used by the Bureau of Standards, but no clear-cut way for practical application of these methods evolved from discussion.

M. M. Baldwin

Subcommittee 5. Editorial.—Since there were no questions to be discussed in an editorial subcommittee meeting, no meeting was held. The committee has completed its editorial duties on the following methods: (1) Proposed Method of Determining Thickness of Units and (2) Proposed Method of Determining Thickness of Specimens.

The following methods are now being processed by the editorial subcommittee: (1) Cold Flex Test (Gruel Test) and (2) Water Absorption, Static.

T. C. Thorstensen

ANNUAL REPORT OF THE ALCA TECHNICAL COMMITTEES

January 15, 1960

Committee appointments.—T. S. Perrin resigned from the Mineral Leathers Committee. R. J. Banner and G. Kimpel were added to the membership of the Committee.

Arthur Kay resigned as Chairman of the Vegetable Leathers Committee, and R. M. Lollar accepted the chairmanship.

W. Windus resigned as Chairman of the Hide Powder Committee, and F. P. Luvisi is now Chairman. G. Daub and G. Downing resigned as members of this Committee, and F. Wagoner and F. L. Collins have replaced them.

M. Bailey, C. Dudley, and A. Hirsch have been added to the Physical and Mechanical Properties Committee.

Methods.—Several notes or slight changes in methods were published for insertion in our Methods Booklet. These were sent to all members with the July and August *Journals*. They were in reference to the saponification and iodine value for oils, the oxidizing mixture for chromic oxide, and hide substance determination in leathers.

The Tannery Effluents Committee, after authorization by Council, published the Methods for Industrial Waste Analysis compiled by them in the October, 1959, *Journal*. The methods were distributed in December for insertion in the Methods Booklet as series M. They are now provisional methods of the Association.

The Proposed Method for Free and Combined Oil of Chrome and Chrome Retan Leather was published in the July, 1959, issue of the *Journal*.

Committees.—The annual reports of the various technical committee chairmen are submitted as part of this report.

The Hide Powder Committee is examining proposed Lot #29. Pending final outcome of results from all committee members, this lot has been given temporary release. The complete results should be ready for publication and official release very soon.

There were no new activities in the Tannin Analysis or Rawstock Evaluation Committees; hence, there is no report.

Minutes of various meetings of the Joint ALCA-ASTM Committee on Leather have been published during the past year and may be found in the February, May, and July issues of the *Journal*.

REUBEN G. HENRICH, *President-Elect*
Technical Committees Coordinator

PREPARATORY AND POSTTANNING PROCESSES COMMITTEE

The work now in progress on drum brine-curing at various packing plants has been followed by chemical analyses of the ash and moisture at the Tanners' Council Laboratory. To obtain a quick end point when the hides have sufficient salt present for cure purposes specific gravity determinations have been made to indicate the salt saturation of the hides. When this method has been established, it may be used to check cured stock readily. Committee work would establish the reproducibility of the method in the hands of different operators. This is called to the attention of the Committee on Cure Evaluation.

Another project at the Tanners' Council Laboratory on developed tests for measuring firmness and temper of fatliquored leathers should be of interest to this committee and should be tried by committee endeavor to establish reproducibility from laboratory to laboratory. These methods are called to the attention of the Subcommittee on Fats and Oils for consideration.

W. T. Roddy
Chairman

OILS AND FATS SUBCOMMITTEE

October 1, 1959

I wish to report on the activities of the Oils and Fats Subcommittee to cover the period between my last report of December 1, 1958, and the above date. No test work has been carried on during this period, and other activities have been at a minimum.

At the Subcommittee meeting at Mackinac Island on June 14 members were asked to present any ideas, information, or new developments that might have some bearing on the several analyses under the jurisdiction of the Subcommittee. Nothing of particular interest was presented.

As you know, the method for free and combined oil of chrome and chrome retan leather was printed in the July, 1959, issue of *JALCA*. Also printed was a request that any ALCA member who had worked out a combined oil determination for other types of leather, submit such information to the Subcommittee. To date no communication of this nature has been received.

Merrill Leach, *Chairman*
Oils and Fats Subcommittee

PHYSICAL AND MECHANICAL PROPERTIES COMMITTEE

December 16, 1959

This Committee of the Association conducts its work only through the ALCA-ASTM Joint Committee on Leather. All work is done through the various subcommittees and sections of the Joint Committee. The chairmen of the Joint Committee, of each subcommittee, and of each section are members of this ALCA Physical and Mechanical Properties Committee. It is through this membership that the American Leather Chemists Association coordinates and carries out its interests in the field of physical testing of leather.

The various subcommittee and section activities, with their chairmen, are noted in the following summary (parenthetical reference is made to the original ALCA Methods):

Subcommittee and Section	Chairman	Study Area	Methods Under Study
II	C. W. Mann	*Sampling and Conditions for Physical Testing.*—	The method for conditioning leather (E1) has been submitted for publication. A procedure for sampling (J1) of side leather is being prepared, and work is being done on sampling methods for small skins.
III, 2	J. Naghski	*Physical Dimensions.*—	Tentative methods have been adopted for area of leather (E2) and width (E5) of leather. Proposed methods have been prepared and submitted to letter ballot on thickness (E4) of leather test specimens and for thickness of leather units (E3).
III, 3	R. Young	*Tensile Properties.*—	The tongue tear resistance method of the ALCA (E10) has been tabled, and the slit tear resistance method of the International Union is under study. The single hole stitch tear (E12) is to be combined with the buckle tear strength method (E11). A study is being made to determine if there is any significant difference between the measurement of

elongation by the bench mark method (E17) and that by the jaw separation method (E17A); the latter will be adopted if the results are not significantly different. The Mullen grain crack test and the ball burst test (E14) are being rewritten for Section approval. Stitch tear (double hole) and tensile strength methods are being rewritten for Section approval.

III, 4 R. G. Ashcraft *Measurement of Water Resistance.*—A method for static water absorption (E30) has been approved by the Section. A spray test for garment leather is under final study within the Section. A method for water absorption of garment leather, using whole skins, is ready for Section approval. A dynamic method for water resistance of heavy leather is under study as are alternate methods for dynamic water resistance (E31) of upper leathers. Work is being done on a method to evaluate the water resistance of finished shoes.

III, 5 R. Stubbings *Surface Characteristics.*—A considerable portion of the huge lightfastness study has been completed. Work to date shows that the Hanovia lamp had little effect upon the leathers studied, under the conditions used, and that the Fade-Ometer gave somewhat more reproducible results than did South Florida exposure at different times of the year. There is a considerable amount of work to be done in interpretation of data.

Methods for the flex testing of finish on upholstery leather and for the cold crack resistance of upholstery (E42) leather finish are being prepared for final submission to the Joint Committee for approval.

Experimental work is under way on crock, scuff, and bleeding tests (E46, E44, K12).

III, 7 A. Hirsch *Mechanical Leathers.*—This Committee is working on a method to determine the area stability of leather in water and oil as well as a corrosion test procedure for leather intended for packings.

III, 8	C. F. Dudley	*Deterioration.*—This Committee is working on methods in the following areas: Heat Stability under Conditions of Pressure and Heat, Storage Stability, and Resistance to Perspiration.
III, 10	M. Bailey	*Miscellaneous Properties.*—This Committee is considering the following procedures: Pipe (E40), Stiffness (E43), Compressibility (E45), a method for measuring break, and a method for shrinkage temperature above 100°C.
IV	M. M. Baldwin	*Research.*—This Committee is studying methods relating to the measurement of electrical conductivity of leather, heat of wetting of leather and other materials, nondestructive tests, and various test methods for evaluating properties related to comfort.

ELL DEE COMPTON, *Chairman*
ALCA Physical and Mechanical Properties Committee

TANNERY EFFLUENTS COMMITTEE

July 3, 1959

I am enclosing herewith a copy of the final report of the Tannery Effluents Committee, two copies of which have been sent to the secretary for checking and forwarding to the printer for inclusion in our Methods Booklet.

Your committee will now be on a stand-by basis, subject to call from Council to set up any additional methods that may appear necessary from time to time.

E. B. THORSTENSEN, *Chairman*
Tannery Effluents Committee

VEGETABLE LEATHERS COMMITTEE

December 28, 1959

The Vegetable Leathers Committee has not been particularly active since the convention. However, I do have from Mr. Blair a copy of some notes which will be worked into a paper to report previous committee work. This paper should come to you early in the New Year.

R. M. LOLLAR, *Chairman*
Vegetable Leathers Committee

STANDARDS AND SPECIFICATIONS COMMITTEE

June 14, 1959

Grand Hotel, Mackinac Island, Michigan

The meeting was called to order by the chairman at 5 P.M. The Chairman reviewed pending old business. The annual report for 1958 was approved. The publication of the report on Sampling of Sole Leather has been delayed, but following the wish of the membership, Mr. Mann will forward the manuscript to the Editor of the *Journal*. The British Standards and Specifications have been circulated among this membership and are now on file with the Chairman. There is no report available on the progress of the work on Determination of Moisture and Grease in Leather. The special study of Nitrogen Determination in Leather Containing Added Nitrogenous Materials, as recommended by this Committee, was not accepted by Council. Instead a note will be inserted in the Methods book under Hide Substance Determination that it will be incorrect in cases where the leather contains added nitrogen in one form or another.

The Chairman has reported to Dr. Kanagy that the membership of this Committee has examined Method 2051 of KK-L-311a (Bursting Strength) and has accepted it.

Mr. Mann requested that this Committee contact the Chairman of the Joint ALCA-ASTM Committee on Physical Testing of Leather in regards to the Shrink Temperature Determination. It was brought out that unless heavy leathers, and especially waterproofed leathers, are very thoroughly soaked in water prior to the determination, the results are unreliable and meaningless. The permissible use of both water and water-glycerine mixture also gives rise to variable results. It was recommended that all heavy leathers should be soaked in water 24 hours prior to shrink temperature determination and that water shall be the only permissible test medium. The Chairman will make the necessary contacts.

The Chairman was re-elected for another term.

The meeting adjourned at 6:30 P.M.

CARL G. TELANDER, *Chairman*
ALCA Standards and Specifications Committee

MINERAL LEATHERS COMMITTEE

July 13, 1959

The Mineral Leathers Committee met on June 14, 1959, at the Grand Hotel, Mackinac Island, Michigan.

It was agreed to have Council insert the following note in reference to the errors in the hide substance determination: "Note: In some cases this may be in error; nitrogen may be added to the leathers through the use of certain resins, polymers, finishes, loading materials, and even tanning materials, and such nitrogen will usually appear as 'Hide substance' by the above method of analysis". This was to be added to 5.2 under B5.

The Analysis of Zirconium was discussed. Wendkos and Somerville published a method of analysis in *JALCA*, **48**, No. 6, June, 1953. A Subcommittee of Mineral Leathers reported very erratic results in *JALCA*, **49**, January, 1954. However, the authors and others have used this method for several years with good results, and it was decided to repeat this work with special emphasis on technique. It was the opinion of Somerville and others that the use of the meeker burner was unsatisfactory since it did not develop sufficient heat for ignition of the precipitate. Therefore, this method of ashing will be omitted in favor of the electric muffle. It is important that 1000° C. be obtained. In the interest of uniformity "several washings" will be specified as "four washings" with 10% hydrochloric acid containing 0.5% of the reagent (p-hydroxyphenylarsonic acid).

Mr. Somerville and Mr. Wendkos will prepare solutions of known strengths but unknown to the committee. They will include a copy of the modified methods to be used. A deadline has been set. Please report by October 1, 1959. If, for some reason, you cannot cooperate, kindly let Mr. Wendkos know so that he does not waste time in making up unnecessary samples.

If we arrive at satisfactory results, we will then ask Dr. Stubbings if he can supply us with weighed samples of a zirconium-tanned, chrome-retanned leather. Fusion or wet oxidation would be optional in this test.

Mr. Kimpel called the attention of the committee to a new book, *Precipitation from Homogeneous Solutions* by Louis Gordon, Murrell L. Salutsky, and Hobert H. Willard. It is published by John Wiley and Sons, Inc. They illustrate methods of obtaining dense precipitates with little coprecipitation of normally slimy voluminous hydroxides of iron, aluminum, and zirconium, as well as many other methods. The technique is not to add the precipitant as such, but to have it slowly generated by a homogenous chemical reaction within the solution. Urea in the presence of succinate or formate is an example.

N. Clifford Benrud, *Chairman*
Mineral Leathers Committee

ABSTRACTS

Chromatography of Phenolic Substances: An Introduction to Paper Chromatography. J. Strachota. *Kozarstvi*, **8**, 248–49, 282–83, 310, 337–38 (1958).—Phenols are the most important raw materials for manufacture of syntans. Commercial phenols vary in composition, and the various isomers and homologs have different numbers of reactive spots and react differently during condensation. Types of phenol alcohols are tabulated. In mixtures of dihydroxy phenols, mono- to tetraalcohols may be formed, and control of condensation is difficult. Chromatography is recommended for analyzing such mixtures. Different kinds of chromatography and conditions for choice of solvent systems are described. If no suitable solvent system can be found in the literature, then an empirical search must be made, guided by the following rules: (1) systems that make detection impossible must be excluded, and (2) polar solvents are better for hydrophilic systems, less polar for hydrophobic. Unknown specimens may be shaken with a mixture of gasoline and water for preliminary orientation. Diazotized, colored compounds of phenols are preferred for detection of different phenols, or the separated phenols may be developed with $FeCl_3$ or ammoniacal $AgNO_3$. Determination of R_F values is necessary. Errors in chromatography and qualitative and quantitative interpretations of chromatograms are described. A bibliography of 108 titles is given. L.M.

Prevention of White Spots on Sole Leather during Tanning. F. Rusicka. *Kozarstvi*, **8**, 250 (1958).—White spots showed up in the third suspender on skins that had received a normal beamhouse process, including deliming with HCl + $NaHSO_3$. Irregular spots on the grain side did not absorb tannin; their depth was 2 to 3 mm. Tannage from the flesh side took place normally. These spots are of microbiological origin. It is believed that bacterial attack took place during storage of the raw hides, rather than in the suspender liquors. L.M.

Prevention of White Spots during Tannage of Sole Leather. J. Jarolimek. *Kozarstvi*, **8**, 347 (1958).—It has now been established that the white spots are caused by *Leuconostoc mesenteroides*, to which Czechoslovak hides seem more susceptible than Argentine frigorificos. The best way to remove them is by a second deliming. Disinfection with Na_2SiF_6, $C_6H_5NO_2$, etc. is about 80% effective. L.M.

Enzymatic Unhairing of Skins. K. Thim. *Kozarstvi*, **8**, 263 (1958).—Unhairing with "Orizon", a preparation from *Aspergillus oryzae*, requires that a temperature of 38°C. be maintained, and therefore the grain of sheep and goat skins may be damaged, even if disinfectant (Na_2SiF_6) is added. The "Ara" liming system is preferred; details of this system are given. L.M.

Enzyme Unhairing of Skins. P. Safarik. *Kozarstvi*, **8**, 381 (1958).—The conclusions of Thim are criticized. Orizon, from *Aspergillus oryzae* or *A. parasiticus*, has thus far been produced only in the pilot plant, and the future commercial product will be easier to apply. A historical review of enzyme unhairing is given. L.M.

Why Color Matchers Differ. Anon. *Textile World*, **109,** 67 (1959); abst. in *Am. Dyestuff Reptr.*, **48,** No. 20, 55 (1959).—In recent experiments at the National Bureau of Standards it was found that the angle of view and differences in age of color matchers must be taken into consideration. C.L.D.

Isolation of Lignin by the Irradiation of Wood. J. L. Garnett and J. W. Merewether. *Chem. and Industry*, **1959,** 1215–16 (1959).—*Eucalyptus regnans* wood meal, previously extracted with ethanol and with boiling 0.12*N* aqueous NaOH, was subjected to varying doses of gamma radiation from a cobalt-60 source. Both lignin and xylan were rendered soluble in ethanol and in boiling 0.12*N* aqueous NaOH; more than 3/4 of the total lignin was soluble at a dosage of $10^{8.5}$ Rads. C.L.D.

Permanent Set, Supercontraction, and Urea-Bisulphite Solubility—The Proton-Transfer Nature of Some Changes in Keratin and the Analogy with Muscle Contraction. P. T. Speakman. *Nature*, **184,** 339–42 (1959).—It is suggested that, in addition to changes in covalent, electrovalent, and van der Waals forces, an increase in the contribution to the resonance hybrid of the peptide groups of the enol form

$$\begin{array}{l} \\ O^-—C=N^+—H \\ \end{array}$$

increases the strength of the hydrogen bonds between peptide groups. This theory is advanced to explain in part permanent set, supercontraction, and urea-bisulfite solubility of keratin. C.L.D.

Stress-Strain Response of Fabrics under Two-Dimensional Loading. Part I: The FRL Biaxial Tester. W. G. Klein. *Textile Research J.*, **29,** 816–21 (1959).—Since the practical applications of fabrics only rarely impose a truly uniaxial stress, as in most cases stresses are simultaneously imposed in more than one direction, a biaxial tester measuring stress in the plane of the fabric gives more information than is obtained by uniaxial testing. Biaxial testing is discussed, and a number of existing testers are evaluated and their shortcomings pointed out. A tester developed at the Fabrics Research Laboratories is described. C.L.D.

A Lesion of the Follicle and of the Fibre of Wool and its Possible Relation with an Excess of Iron in the Forage. G. Gonzalez, J. Garcia, and E. Fernandez. *Nature*, **184,** 559–61 (1959).—Sheep which graze in certain regions of the Iberian Peninsula lose their wool progressively; degeneration of the follicles is associated with this condition. It is postulated that this condition may be due to abnormally high iron content of the soil and vegetation. C.L.D.

The Shape and Cause of Wool Crimp. O. K. Dobozy. *Textile Research J.*, **29,** 836–39 (1959).—A mathematical treatment of the curves of crimped wool is given. It is suggested that the curves indicate that it is very likely that the crimpiness of the wool fibers is directly proportional to the swelling of one part of the cortex, while inversely proportional to the swelling of the other part. Crimpiness of wool is therefore caused by the shrinkage of part of the cortex and the swelling of another part. C.L.D.

Disorganization of the Secondary Structure in Proteins Exposed to Ionizing Radiations in the Solid State. P. Alexander, L. D. Hamilton, and K. A. Stacey. *Nature*, **184**, 226–28 (1959).—Changes produced by irradiating solid crystalline bovine serum albumin with 2 MeV. electrons in the absence and presence of oxygen were studied. In the absence of oxygen, the first effect of irradiation is to disorganize a large part of the molecule as a result of a breakdown of many secondary valency bonds; the irradiated molecule has essentially the same molecular weight as the non-irradiated, but its shape has been changed (which produces an increase in frictional resistance in the ultracentrifuge) and 5 disulfide bonds normally hidden are revealed. Further irradiation renders the protein molecule insoluble in water but soluble at high and low pH values and in salt solutions; the molecule has a greatly increased molecular weight, since cross links (not hydrogen bonds or disulfide bonds) are formed between the original molecules. Further irradiation renders the protein insoluble even in salt solution, with extensive alterations involving about 5% of its amino acid residues. The amino acids vary in sensitivity to the irradiation. Main chain polypeptide bonds are not broken. The presence of oxygen during irradiation does not alter the first stage of "opening up" or the destruction of amino acids. However, the protein is rendered insoluble in water at lower doses, and main-chain breaks may occur. C.L.D.

Analysis of Stress-Strain Curves of Soda-treated Wool Fiber. G. Satlow. *Textile Research J.*, **29**, 841–43 (1959).—Stress-strain curves of wool fibers pretreated with 0.1*N* NaOH were determined up to 50% extension. The results support the theory of Kessler and Zahn (*Textile Research J.*, **28**, 357–58 [1958]) that a disulfide exchange in the wool protein takes place during alkaline treatment, in which intrachain disulfide bonds are transformed into interchain disulfide bonds. C.L.D.

Molecular Shape and the Physical Properties of Mucin. R. A. Gibbons. *Nature*, **184**, 610 (1959).—Previous work on epithelial mucin has indicated that it contains neutral mucoids of the blood group substance type with a random coil, which represent a homologous polymer series. A theory correlating sedimentation coefficients and molecular weights for random coil molecules is developed; it is shown that experimental data on the mucoids agree with the theory. Further evidence in favor of the view that epithelial mucin is a random coil polymer is found in the behavior of its aqueous solution on addition of a third component. C.L.D.

Gelatin and Glue Research. A. G. Ward. *Nature*, **184**, 862 (1959).—A review is given of the papers presented at the seventeenth meeting of the Research Panel of the British Gelatin and Glue Research Association (June 25, 1959). I. "Present Position in Gelatin and Glue Research" by A. G. Ward. II. "Formation and Structure of Gelatin Gels" by J. W. Janus. The rigidity of the matured gel, the melting point, and the setting time from the sol state depend on solution pH. Setting may occur in a short time even at room temperature, but gel rigidity increases over a long period at 0°C.; the melting point is much less influenced by low-temperature maturing. Interference with setting can be secured with alkaline Cu solutions, which are presumed to interact with the >CO groups of the backbone. An interaction between guani-

dinium groups and the backbone is postulated to explain the early stage of setting. The continued growth of rigidity at low temperatures is exp'ained by a reversion to the helical structure; optical rotation changes support this view. III. "Swelling of Starch" by R. Collison and G. Elton. IV. "Measurements on Gelating Gels at High Frequency" by D. D. Carruthers. C.L.D.

Routine Methods for Determining Quality in Merino Wool. P. L. leRoux. *Nature*, **184**, 917 (1959).—The root portions of samples of wools which had been appraised for quality by wool experts were used for the following determinations: plasticity, total S, tyrosine, and solubilities in alkali and in urea-bisulfite. Results indicated that all these methods may be used to characterize wool quality. The better wools showed higher plasticity, tyrosine content, and solubilities in alkali and in urea-bisulfite, and lower S content. The relationship between quality and solubility in alkali was also valid for whole wool staples, although the tests were not so sensitive as with the root portions. C.L.D.

Influence of Dietary Protein Percentage on Growth of Wool. K. A. Ferguson. *Nature*, **184**, 907 (1959).—No statistically significant difference in growth of wool between groups of sheep fed isocaloric diets of different protein content was found. C.L.D.

Action of Sulfuric Acid on Wool. III. Isolation and Analysis of Three Preparations from the Wool Fibre. R. L. Elliott, R. S. Asquith, and D. H. Rawson. *J. Soc. Dyers Colourists*, **75**, 455 (1959).—In continuation of previous work (*J. Soc. Dyers Colourists*, **74**, 176 [1958]) three residual membranes were prepared by treatment of wool with 47% H_2SO_4 at 29°C. for 5 days (Membrane A), with 98% H_2SO_4 at 29°C. for 4 days, followed by extraction with 10% Na_2CO_3 at room temperature (Membrane B), or with boiling 0.05*N* KOH for 105 minutes (Membrane C). The complete amino acid compositions of the three membranes were determined. Membranes C and A may be identical. All three have a low content of amino acids with long side chains. Membrane A has an exceptionally high cystine content. Histologically, Membrane A surrounds the cortex of the fiber, and Membrane B lies below the scales. C.L.D.

A Rapid Determination of Chromium in Wastes in the Presence of Organic Matter. A. Blazej and E. Markusovska. *Veda a Vyzcum v Prumyslu Kozedelnem*, **4**, 117–25 (1958).—The methods of Kubelka and Wagner, Feigl *et al.*, Gagliardi, and Küntzel are critically discussed. Oxidation by $KMnO_4$ is preferred to $HClO_4$. Heat 25 ml. of solution containing 1 g. Cr in 1000 ml., with the addition of 20 ml. of 50% H_2SO_4. Add a 0.5% solution of $KMnO_4$ in 1-ml. increments, waiting for decolorization after each addition. When a brown precipitate appears, add 2 ml. and boil 3 min. If the solution clears, continue the addition until a permanent precipitate of MnO_2 is obtained. Then add HCl (1:1), slowly, until the precipitate disappears. Add 50 ml. water, and boil for 5 min. Add 10 ml. of 0.5% $NaHCO_3$ solution, and heat until Cl_2 is expelled completely, as shown by a negative test of the vapor with KI paper. Then titrate the solution iodimetrically or with Mohr's salt. L.M.

A Contribution to the Occurrence of Molds in Tanneries. P. Safarik and E. Vintrova. *Veda a Vyzkum v Prumyslu Kozedelnem*, **4**, 93–100 (1958).—The occurrence of molds in a sole leather tannery was studied by exposing plates of Czapek-Dox agar for 5 min., once a day for 2 months, at 5 locations. The microflora of tanneries is said to be characteristic, and very similar in different countries. The various species of molds that were identified are listed; of these, 60% were various *penicillia;* 17%, *Aspergilli;* 12%, *Paecilomyces;* 6%, *Rhizopus; and* 4%, *trichoderma;* other genera were found only occasionally. Among the yeasts, *Torula, Rhodotorula,* and *Saccharomyces* were most abundant. Most of the molds can split tannin. Contamination was heaviest in the hide cellar, followed by the beamhouse and the suspender yard; the finishing department was only lightly contaminated. Some microorganisms noted as typical of tanneries by other workers were not found. L.M.

The Determination of Water Permeability of Shoes. K. Tuma and M. Culrova. *Veda a Vyzkum v Prumyslu Kozedelnem*, **4**, 101–15 (1958).—A last wrapped in weighed filter paper is placed in a weighed shoe. The shoe is placed in colored water and shoe and filter paper are reweighed at intervals. Gain in weight of shoe gives water absorbed, gain in weight of filter paper gives water penetrating the shoe, and spots on filter paper show the points of penetration of the water. Generally entrance of water takes place at the junction of sole and upper. Seventeen pairs of heavy shoes were tested. Greasing reduces water absorption by 30–40%. High penetration is more often due to manufacturing defects than to characteristics of the leather. Time for penetration is 155–174 hr. for best ski boots, and this is about doubled by greasing after manufacture. For ordinary work shoes a penetration time of 30 to 90 min. is considered satisfactory. L.M.

New Method for the Determination of Hiding Power of Pigment Colors for Leather. D. Kokes and K. Motycka. *Veda a Vyzkum v Prumyslu Kozedelnem*, **4**, 65–76 (1958).—Hiding power is measured by determining photometrically how much of a 0.1% dispersion of pigment is required to reduce the transparency of a solution to 20% of its initial value. A second method is to spray a 5–15% dispersion of pigment in 10% casein solution onto a weighed glass until the transparency is reduced to 20%, and then weigh the glass plus dried film. The precision of the first method is ±2% and of the second ±5%, but results by the second method agree better with actual tests on leather. A Zeiss Luxmeter is used in both methods. L.M.

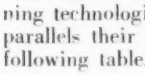
The Formation and Development of the Fibrous Structure of the Skin. V. Kubelka. *Veda a Vyzkum v Prumyslu Kozedelnem*, **4**, 77–92 (1958).—Research on living hide fibers is still in the beginning stage. The relationship between the principal components—cells, amorphous intercellular substance, and fibers—is not clear. Cells are most important from the genetic point of view, as they produce the intercellular substance, which is eliminated from the cells in an unknown way. Protofibrils are formed outside the cells, in the intercellular substance—and probably from it. Protofibrils unite to form fibrils; the process resembles crystallization. This process has recently been explained in part by electron microscope studies, with direct magnifications of 50,000 (photographically up to 200,000). Protofibrils formed from collagen

solutions outside the cell have been found to be identical with protofibrils formed *in vivo*. The theory of formation of fibrous macromolecules of collagen by mutual attraction of rodlike polypeptide molecules existing in the intercellular substance is given. L.M.

The Use of Ready-for-tanning Chrome Products. H. Spahrkäs and H. Schmid. *Das Leder*, **10**, 145–49 (1959).—Normal tannery practice is to dissolve powdered tanning extracts with heat, then to dilute concentrated liquors and age them for a few days to promote uniformity. In laboratory tests, however, it was found that when the powdered extract was added directly to the tan drum, the chrome was taken up rapidly, distributed uniformly, and the leather was full, uniform in color, free from spots, and had a fine grain. To study this behavior further, solutions of Chromosal B (Bayer) containing 2.6% Cr_2O_3 per liter were prepared both at 20°C. and at boiling. The basicities at which precipitation started were determined by titrating 200-ml. portions of the solutions at 20° with 3*N* soda solution, adding 2 ml. of soda solution every 10 seconds. These basicities were, for the solutions prepared cold, 110% (pH 7.5) at once and 60% after aging for 24 hours. Most of this decrease occurred during the first 6 hours. For the solutions prepared hot, the precipitation basicity at once was 70% and after 24 hours, 60%. Solutions prepared cold were strongly sulfate-masked for several hours, but the sulfate complex will gradually decompose in dilute tan liquors as tanning proceeds. It is therefore possible for the tanner to start the tanning with strongly masked, anionic chrome compounds of low astringency and end with reactive, cationic compounds. Several commercial products were found to be sulfate-masked. Products having the character of self-reduced liquors were somewhat more stable than pure chromium sulfate products. Decrease in Glauber's salt content decreased stability (masking). Concentrated solutions were more strongly masked than dilute solutions. A series of concentrations of a commercial chrome liquor was prepared by boiling each solution for 5 minutes, then aging it 24 hours. After each was diluted to contain 2.6% Cr_2O_3, the solutions were titrated at once at 20° with 3*N* soda. Precipitation basicity decreased from 105% (pH 7.6) in the solution containing 18% Cr_2O_3 to 65% (pH 5.3) in the solutions containing 10% or less of Cr_2O_3. An increase in temperature increased rate of decomposition of the complex. A basic chrome liquor diluted to 2.6% Cr_2O_3 had a precipitation basicity of 65% if aged one hour at 40°C. before titration but of 95% if aged at 20°. During a tanning test with Chromosal B the chrome concentration in the liquor decreased rather uniformly during the 8-hour tanning period if the Chromosal B was not dissolved before addition, but if it was prepared hot by the usual method, the concentration decreased more slowly than the above for three hours, then decreased rapidly for the next 2.5 hours during neutralization, but then showed little further decrease. I.D.C.

Affinity of Tannins and Tanninlike Substances for the CO-NH Group in Polyamides. W. Grassmann, H. Endres, M. Oppelt, and H. El Sissi. *Das Leder*, **10**, 149–56 (1959).—Theories of vegetable (phenolic) tannages are reviewed; 44 references. There is general agreement today that tannins unite to peptide groups of skin through hydrogen bonds by a mechanism analogous to that by which phenolic substances combine with polyamides. The use of polyamide instead of hide powder for tannin analysis has been pro-

posed. In the present work a chromatographic study was made of the behavior of twenty 2-ring phenolic compounds with the polyamide Perlon L (Hoechst). Eluting was done with acetone, methanol, 1:1 water-acetone, and 1:1 water-methanol. Both R_f and R_m values were calculated. $R_m = \log (1/R_f - 1)$. Affinity for polyamide was directly related to the number of phenolic hydroxyl groups in the compound. R_f values (methanol-water) were as follows: with 1 OH group, 0.22–0.24; 2 OH groups, 0.13–0.21; and with 3 or 4 OH groups, 0.00. The type of group or bond joining the 2 aromatic rings was of little importance. R_f values (acetone-water) or 4,4′-dihydroxy derivatives of several compounds were as follows: azobenzol, 0.51; diphenyl, 0.56; diphenylsulfone, 0.57; benzophenone, 0.62; stilbene, 0.62; and diphenyldimethylmethane, 0.63. Increase in size of the aromatic portion of the molecule increased affinity. For example, the R_f value of phenol was 0.66 and of naphthol, 0.28. Two or more OH groups were not always equal for steric reasons. Both OH groups of 4,4′-dihydroxydiphenyl formed hydrogen bonds with polyamide, but 2,2′-dihydroxydiphenyl formed only one hydrogen bond to polyamide because of formation of an intramolecular hydrogen bond between the two OH groups.



where B represents the benzene ring of the phenol. The same factors that affect elution of phenol from polyamide are evident in tanning technological behavior. That the binding of phenols to polyamides largely parallels their tanning action on hide substances is shown by the data in the following table.

Phenolic Compound	T_s	Tannage	R_f Water-Methane	R_f Water-Acetone
2-hydroxydiphenyl	59°	not tanned	.22	.62
4-hydroxydiphenyl	62°	not tanned	.21	.64
2,4-dihydroxybenzophenone	62°	slightly tanned	.20	.65
4,4′-dihydroxydiphenylmethane	71°	moderate	.15	.56
2,4-dihydroxydiphenylmethane	75°	well tanned	.16	.57
2,4,2′,4′ tetrahydoxydiphenylmethane	83°	very well tanned	.00	.00
2,4-dihydroxybenzhydrol	90°	very well tanned	.12	.20

I.D.C.

The Strength Characteristics of Leather. E. Baumann. *Das Leder*, **10**, 156–62 (1959).—German, English, French, and American official methods for testing the strength of leather are briefly described. A comparison of four methods was made using three skins from each of 12 types of leathers having thicknesses ranging from 0.5 to 3.5 mm. For each test, five specimens were cut from each skin. Tensile strength was measured with specimens of two sizes, 100 x 25 mm. (60 x 15 mm. test area) and 40 x 10 mm. (20 x 5 mm. test area). Tear strength was measured by the one-hole stitch tear method and by a newer method that is now being investigated by the International Commission on Physical Testing of Leather. In this last method developed by Baumann (Bally Schuhfabriken in Switzerland), a 50 x 20 mm. specimen with a slit or a 5-mm.-wide opening in the center is fastened over two special

hooks attached to the jaws of a tensile tester (diagrams without dimensions are given of specimens and hooks). Tensile strengths with the narrow and wide specimens were in good agreement, and coefficients of variation were about the same except with two of the leathers. Narrow specimens gave slightly higher tensile values than wide specimens if the leather was thin but slightly lower values if the leather was thick. The narrow specimen has the advantage that more pieces can be cut from a given sample, but it does not permit an exact determination of stretch at break. There was good agreement between results by the two tear methods, but the new slit method was more precise and preferable. The coefficients of variation of the results by the stitch tear method ranged from 5.3% to 22.9% (averages for the 12 leathers) and from 4.8% to 16.6% for the new method. For control testing, the new slit tear method is sufficient to characterize the leather. I.D.C.

Third International Colloquium of Leather Chemists. M. Radil. *Kozarstvi*, **8**, 311–12 (1958).—This colloquium, held in Moscow June 24–28, 1958, was attended by chemists from the USSR, Bulgaria, Hungary, East Germany, red China, Mongolia, Poland, Roumania, and Czechoslovakia. Leather finishing was discussed. In China, casein is being replaced up to 40–50% by hide glue, or wholly by silkworm cocoon protein. Modified caseins (see succeeding abstracts), finishing leather with buffed grain, and control of finishing were specially discussed. Stability of finished leather to low temperatures and to common solvents must be improved. L.M.

Leather Finishing with Pigment Finishes in Czechoslovakia. M. Radil. *Kozarstvi*, **8**, 326–29 (1958).—A lecture. Casein pigments are used only for finishing box calf and glazed kid. Both inorganic and organic pigments are used. Organic pigments have been produced in a pilot plant by precipitating aniline dyes on an inorganic carrier with amino resin. They are resistant to solvents and have good hiding power. Modified caseins similar to Luron binder U and UW, Icafix, and Calfaplast are made by reacting casein with vinyl products—chloroprene, methyl methacrylate, or ethyl methacrylate. The casein is first dissolved in triethanolamine. Films containing modified casein can easily be fixed by HCHO and possess good elongation. While ordinary casein film elongates only 2%, or 3% if plasticized with 33% sulforicinoleate, these modified casein films give elongations of 9 to 26 alone, and up to 160% if plasticized. Modified caseins are still in the pilot-plant stage. For preservation of casein pigments, *p*-Cl-*m*-cresol has been found best. Thirteen basic shades are being produced, containing 12–23% solids, applied at densities of 1.04–1.07. The leather is generally given two pigment brush coats, one or two spray coats, glazed, sprayed with a casein-wax coat, and glazed. Finishing with nitrocellulose pigment finishes is done only for spraying suede, using a very dilute solution. Combined casein, resin, and nitrocellulose finish is applied to garment and pocketbook leathers, using casein and resin in the ground coats and nitrocellulose for the top. For nitrocellulose pigment finishes, a medium viscosity nitrocellulose is used, with castor oil, tricresyl phosphate, diethyl or dibutyl phthalate, and sometimes tributyl citrate. Casein-resin pigment finishes are most widely used. Shrunken grain is produced on goat, pig, and steer hide by adding special syntans during tannage. Pigskin straps for summer sandals are embossed with a hot cylinder. A new type of suede from steerhide or splits (Rex Velour) has a two-tone effect achieved by tear-

ing out uncolored collagen fibers from the flesh side. Angora velour is produced from buffalo hides, which give very long fibers by tearing. Production of patent leather has been resumed, using nitrocellulose-glytpal resin daubs and pure linseed oil lacquers. Isocyanate resins have given only indifferent results. Top spray coats of dissolved polymethacrylates, polyethacrylates, and methyl and butyl methacrylates did not adhere well to casein-resin finishes. Better results were obtained with butyl methacrylate polymerized in toluene with added nitrocellulose; it gives an elastic, light-stable film of good aging characteristics which can be applied to casein-resin finishes or even to straight casein finish if further diluted with toluene. The nitrocellulose sprays for suede have recently been replaced by N-alkoxy-methyl polyamides with epoxy resins added. These polyamides are stabilized at higher temperatures by adding H_2SO_4, oxalic, maleic, or phthalic acid as catalysts. Best results have been obtained with polyamide from polycaprolactam modified to 28–30% -CO-NH- groups. Epoxy resin is added to permit stabilization at temperatures below 100°C. Epoxid 2100B is stabilized at 40°C. for 60–120 min. The ratio of pigment to resin is 0.25–0.45 to 1, and the ratio of dry polyamide to epoxy resin is 1 to 0.5–0.7. The product sprayed on suede contains 15–18% solids. The leather has even shade, fine nap, and silky feel. Pigskin nubuck, especially black, has given good results. Box calf and glazed kid have been produced on the pilot-plant scale using casein-resin undercoats and straight casein—or, better, modified casein—top coats, which can be glazed. L.M.

World State of Finishing Leather by Pigment Finishes. V. Pektor. *Kozarstvi*, **8**, 330–35 (1958).—An address. Casein for finishes should be soluble at pH 8.5, with low fat and acidity. For white and pastel shades casein should be fixed with acetic acid at pH 5. The hydrophilic behavior of casein is lowered by adding shellac, melamine resins, natural or replacement waxes, albumins, formamide, di- or triethyleneamine combined with stearic or acetic acids, alkyleneimines, and propanedisulfodiethyleneimide. For plasticizing casein films, low-sulfated, nearly neutral castor, neatsfoot, or linseed oil, without electrolytes, is best. The limiting percentage of plasticizer on dry casein is about 30%; for a glazing finish, part of the oil should be replaced by glycerol or polyglycol. Preservation with 1.5–2.5% of *p*-CL-*m*-cresol is best, not that this is the best fungicide, but it has least effect on the stability and shade of the finish. Pigment pastes without binders, of 0.0005–0.0001 mm. particle size, have been newly developed in England. The dyes used in finishes must be stable to alkalies and HCHO, and not over 10 g. per liter should be used. So-called aniline leathers are dyed subsequently with anionic and cationic dyes, so that a fine pigment is deposited on the grain. It is possible to finish 15% to 20% of the skins in this way. Nitrocellulose is rarely used alone but frequently as a surface spray to make the surface hydrophobic and impart a dry feel. The solvents used should partially dissolve the underlying coat and should form azeotropic mixtures with water. Diamyl or dioctyl phthalates probably are the best plasticizers; tricresyl phosphate, though effective, is poisonous and should not be used. Dissolved polyacrylates are also good plasticizers; polybutyl acrylate dissolved in toluene is used in Czechoslovakia. Water dispersions of nitrocellulose (e.g., Hydrolac) are promising. Resin finishes are described. Diene resin finishes (copolymers of butadiene with methyl methacrylate) fill the grain better but must be stabilized. The resin dispersions should have 0.0005–0.0006 mm. particles. Good penetrating resin dispersions coagulate at 85% concentration; for good grain filling they

should coagulate at 45% concentration. Resin finishes generally are thermoplastic, and the leather is smooth-plated instead of glazed. More recent types (e.g., Eukasolbinder) have a higher melting point and can be glazed. In Eastern Germany corrected grain leathers, chiefly steer and pig, are filled to make buffing easier. Dicyandiamide-HCHO resins with molar ratio of 1:4.5 are suitable, and they are more stable in aqueous dispersions than condensates with molar ratio of 1:3.6. Higher degree of condensation gives resins with greater particle size. Czechoslovak experience with Retingen R6 (Chemtan R6) is said to have been not very good. In Czechoslovakia leathers are filled with Otamol (water solution of cationic dicyandiamide-HCHO resin) and Umacol C (water solution of amphoteric dimethylol urea resin). They condense in the leather. Plastan, similar to Otamol, is used in Hungary. Coprecipitation of cationic resins and syntans is also used for filling. Thermoplasticity and solubility in solvents are the principal drawbacks of resin finishing. Masner (Czech. patent no. 86796) diminishes the solubility by irradiating finished leather with cobalt 60. Certain proprietary finishes are mentioned, e.g., Kasikaplastbinder, melting above 200°C., and Cellsika Glanztop, resistant to solvents, especially acetone. Another way to overcome these drawbacks is by use of modified proteins, i.e., copolymers of proteins with acrylic acid derivatives. Alcoholic solutions of alkoxypolyamides are used for finishing in Poland. The best plasticizer for these is polyacrylate. Appretiermittel 800A and 800B, and Ledergrund C are similar products. The stabilization of alkoxypolyamide resins is catalyzed by lactic or citric acids; complete stabilization is achieved at 100°C. in 5–6 min. BCI Nylon 818D, produced in the U.S., is a water dispersion of a polyamide. Patent leather made with isocyanates is more resistant to cold than ordinary linseed oil patent. Manufacture of shrunken grain leather from pigskins; perfumed garment, glove, and morocco leathers; and machinery for finishing leather are described. L.M.

Modified Casein. F. Belohradsky, L. Blajez, M. Kulhanek, and V. Navratil. *Kozarstvi*, **8**, 361–63 (1958).—In making modified caseins by heteropolymerization of casein with vinyl compounds, different proportions can be used, but enough casein must be present to permit hardening the product by formaldehyde. The films are much softer and more suitable for bottom coats in leather finishing. Modified casein is very useful for finishing pasted shoe upper leather with corrected grain and can replace up to 50% of the resin dispersions normally used. L.M.

Influence of Fatliquoring and of Different Additives on Dyeing of Leather. V. Pektor and J. Ondracek. *Kozarstvi*, **8**, 364–67 (1958).—Influence of anionic, cationic, and nonionic fatliquors and additives on dyeing Cr leather has been studied, with special reference to utilization of dye, striking-through, evenness, intensity of shade, and lightfastness. Among anionic additives Biltan is superior to Kortemol NNO, and Syntamin A is superior to Katexol among cationic additives. Cationic additives impart much better light stability than anionic ones, as well as better exhaustion of the dye bath. Nonionic additives (Eryfor O) give more even dyeing only at the pH of neutralized Cr leather. Intensity of shade is best with cationic additives and very good with nonionic, using anionic fatliquors. L.M.

New Method of Drying Leather. B. Plechac. *Kozarstvi*, **8**, 368–71 (1958).—Paste-drying of Cr leather to 11–16% water requires a tunnel capable

of operating at 80°C. and 20% to 90% relative humidity. Removing 1 kg. water from leather theoretically requires 200 g. air and 1200 cals., equal to 2.13 kg. steam at 3 atmospheres. In practice 2.5 kg. steam was required. Types of drying tunnels are described and illustrated. L.M.

Tanning of Glove Leather by Means of Alkyl Sulfochlorides. J. Jakl and J. Strnad. *Kozarstvi*, **8**, 360–61 (1958).—Alkyl sulfochlorides produced by treating paraffins with 22 to 27 C atoms with Cl_2 and SO_2 are used to tan glove leather, replacing the white tawing process. The skins are pretanned overnight with HCHO and $NaHCO_3$ at pH 7.9–8.1, then pressed, and treated in a drum at 45°C. with a mixture of 15–20% sulfochloride, 5–6% Na_2CO_3 and 0.6% Syntanon L (anionic detergent), on the pressed-skin weight, added immediately after mixing. The detergent emulsifies any free hydrocarbons in the sulfochloride. To avoid saponification of the alkyl sulfochloride, 50°C. must not be exceeded. The skins are drummed 3 hr., then 2% Slovanol EL (nonionic detergent) in 30% water is added at 45°C., and drumming is continued 1 hr. longer. The skins are then dried at 42°–45°C., washed at 40°C. with 5% trichlorethylene and 2% Slovasol in 500% water to remove free paraffin, struck out, washed lightly, and fatliquored for 1 hr. with 1.5% Lipaminlicker O, 10% kaolin, and ultramarine to improve the whiteness, in 400–500% float at 45°C. The leather is then set out and dried. L.M.

Amino Acids and Chemical Bonds in Hide Protein. V. Kubelka. *Veda a Vyzkum v Prumyslu Kozedelnem*, **5**, 7–21 (1959).—Practically all the amino acids of collagen have been identified; 22 of them are described. Glycine, arginine, proline, hydroxyproline, alanine, and lysine make up 75.6% of collagen. Different forms of amino acid bonds in collagen are described. Peptide bonds can exist in lactam, lactim, and enol forms, which form different dipoles and, therefore, have different reactivities. Mesomery in peptide bonds is explained. Ester, arginine, ester-peptide and perhaps pyrrole, dioxypiperazine, and ureide bonds exist in collagen. L.M.

The Influence of Tannery Wastes on the Recipient Stream. K. Jansky, P. Safarik, and J. Svek. *Veda a Vyzcum v Prumyslu Kozedelnem*, **4**, 127–41 (1958).—The self-purification of tannery sewage in the Drevnice River, heavily contaminated with municipal wastes, has been studied by chemical, biological, and bacteriological methods. After the sewage, from which 80% of the solids had been removed by sedimentation, was diluted 30- to 175-fold in the river, no increase in alkalinity or BOD was found; only the brown discoloration caused by tannins was evident. Coli titer showed a diminished fecal contamination. By determination of biological toxicity at 50- and 100-fold dilution, no decrease in self-purification capacity of the river was observed. The self-purification was estimated by determining the Phelps-Streater reoxidation constant, K_1, and re-aeration constant, K_2. Values of $K_1 = 0.7$–0.8 and $K_2 = 1.9$–2.1 were found, compared to normal values of $K_1 = 0.1$ and $K_2 = 0.2$; hence self-purification was more rapid than normal. The Svit Tannery in Gottwaldov-Malenovice produces about 580 cu. m. of sewage per day, or 20.5 l. per sec. during the working day. This effluent had BOD 1364 mg., and $KMnO_4$ No. 808 mg. O per l., and no free O_2. The river flow was 750–3500 l. per sec., and the current speed was 0.15–0.20 m. per sec. Determination of the intensity of self-purification by determining K_1 and K_2 is advised in all cases when construction of a purification plant is contemplated, to avoid building unneeded plants and the resulting heavy economic losses. L.M.

Use of Additives in Dyeing Glove Leather. J. Jakl. *Kozarstvi*, **8**, 264–67 (1958).—Additives can be used at different stages. Kortamol NNO (naphthalene sulfonic acid–HCHO–neutralized condensate) is best used before dyeing to level pastel shades; in brush-dyeing it may be used at a maximum concentration of 0.5%. Danger of marbling is enhanced if over 1% of NH_4OH is used; 0.4% gave no marbling. A procedure is described for dyeing kid glove leather with cationic detergents. The leather is neutralized and treated with dye and ammonia. Then after more ammonia is added, the leather is treated with formic acid and a cationic fatliquor, followed by basified Cr alum. Finally a surface-dyeing is accomplished with dyes, followed by formic acid. Marbling is less pronounced compared to normally dyed leather with Kortamol NNO. An amino resin has been used as cationic additive but tends to give drawn grain and less stretchable, cracky, glove leather. The resin works better for upholstery leather, especially for black.

Biltan has been found superior to gambier for light vegetable retanning; it makes for easier buffing, but the cationic surface activity of the leather is lessened considerably. Better results are obtained by dyeing with two-thirds of the dye, then treating with the amino resin, preferably combined with retannage with 45% basic Cr alum, and finally surface-dyeing with the remaining third of the dye. Good use has been made of amino resin in brush-dyeing. Anionic-fatliquored leather is brush-dyed twice, set out after each dyeing, then brushed with a 1% solution of the resin, and given further brush-dyeings. Except for blacks the shade tends to be uneven. Some black leather has been brush-dyed before fatliquoring, as described above, then left folded overnight after fixing with formic acid, then drummed with 250% water and 0.5% amino resin at 70°C. for 20 min. The anionic fatliquor is added to the same bath. No precipitation of fatliquor was noted, as absorption of the amino resin was complete. Fixation of dye was not complete, giving a desirable gray tone on the flesh side. Tests with Bastamol FJ as cationic agent were not altogether successful; applied after brush-dyeing it gave uneven shades except with black. Better results were obtained with a mixture of Bastamol, Cr alum, and $NaHCO_3$, but 33% basic Cr liquor without any Bastamol gave still better results. Dyeing for pastel shades is being done on dried-out leather. Anionic fatliquoring before drying is being done with addition of anionic saponates (Syntapon L-type) to lower the surface tension. Good results have been obtained in fatliquoring kid leather with sulfated neatsfoot oil and Eryfor EL (nonionic, ethylene oxide–type detergent), added after exhaustion of the sulfated oil, or with sulfated neatsfoot oil followed by cationic agents (Syntamin A, KL 13). Another good detergent is ETM, containing Na naphthenate soaps. The sulfated neatsfoot oil–Eryfor fatliquor gave no marbling after dyeing; the others did. Retannage with 2.5% Biltan on the shaved weight gave fuller leather without sacrificing softness and stretchiness, but the negative effect on intensity of dyeing is a disadvantage. Treatment of chamois leather after bleaching with 6–8% Biltan on the dry weight produced leather that could be colored through and buffed better, resulting in gloves that did not get felty even after repeated washing. L.M.

CORRECTION

In the January number, in line 3 of the next-to-the-last paragraph on page 28, the amount of solvent should be 1000 grams instead of 100 grams.

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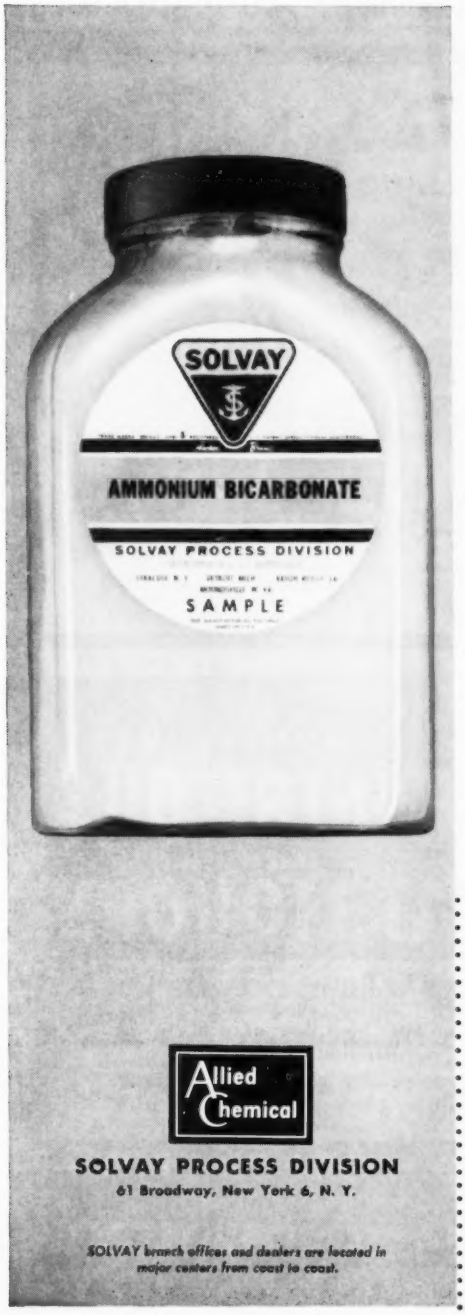

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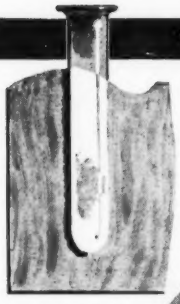

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"Z" AS IN ZEBRA

A side leather tanner told us this interesting process story recently. Troubled with a natural grease problem in his sides, he attempted to correct the situation by expensively solvent degreasing the stock early in the process.

The Other Side of the Coin

After such treatment the blue stock still oozed grease as it was laid on pallets. It was necessary to wring twice to obtain even passable splitting and he could not hold his weights on the splitting machine. Subsequent steps in the process were troublesome because of grease, and the finished sides were down-graded on the table.

A pack was run in which the solvent degreasing was eliminated. In its place ½% Seabomul "Z" (based on limed weight) was added with the first tan feed. By evenly dispersing the natural grease throughout the sides, he was now able to wring properly on the first pass and weights were held in splitting. The finished stock was grease-spot free and ready for full value merchandising.

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Sounds like a success story — and it is!! As more and more cattle are force-fed weight builders in the form of soya-bean and tallow derivatives, the tanner's problem increases. Sooner or later, if you tan sides or splits, you'll face the problem in your tannery. When you do we suggest you look to Seabomul "Z" as an easy, economical way out of the grease dilemma.

If you're troubled with grease now, we suggest you discuss with us the type of leather you are running. We'll promptly send a sample of Seabomul "Z" with detailed instructions for its use on your leather.

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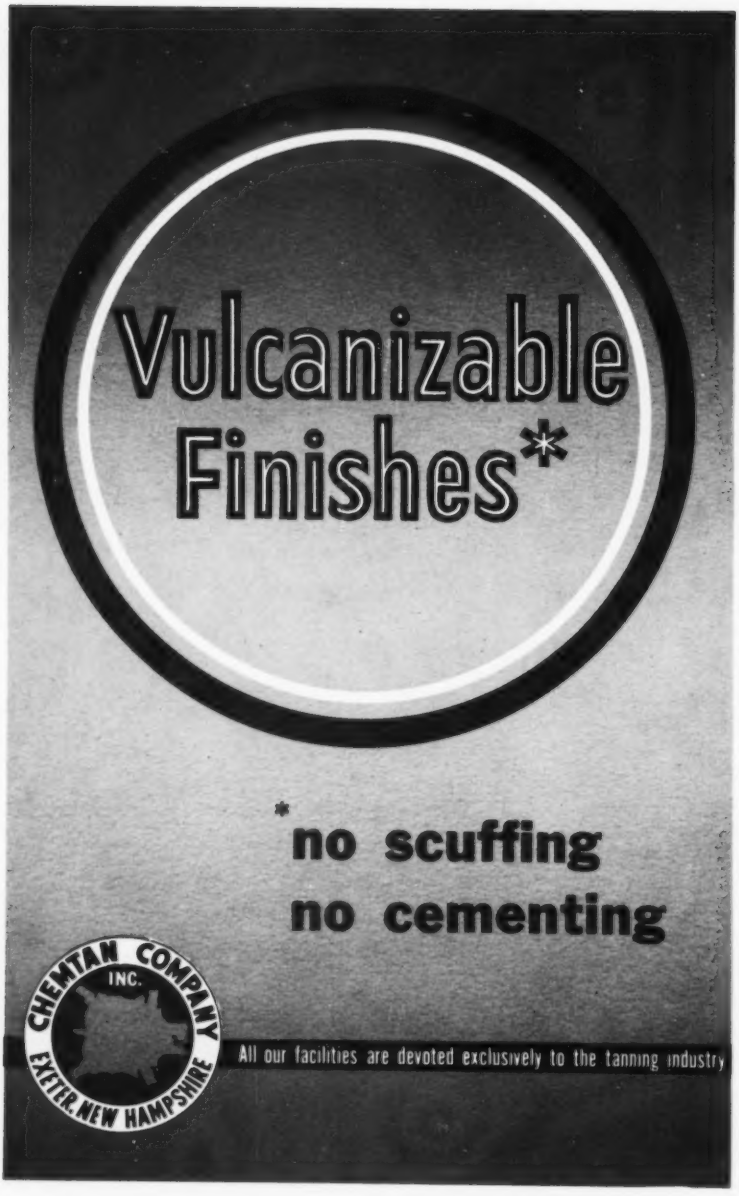
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